UNIFIED THEORY OF A.C. AND D.C. HOPPING CONDUCTIVITY IN DISORDERED SYSTEMS

by

STEPHEN SUMMERFIELD

A thesis submitted to the University of Warwick
for admission to the degree of Doctor of Philosophy
September, 1982.

TABLE OF CONTENTS

APPENDIX A ANALYTIC APPROXIMATION TO R-INTEGRALS OCCURING IN CONDUCTIVITY FORMULAE

LIST OF FIGURES

ACKNOWLEDGEMENTS

First and foremost I thank Professor P.N.Butcher for the excellent supervision I ~~recieved~~ received during the course of work that led to the preparation of this thesis. I would also like to thank the members of the theoretical physics group at the Department of Physics for many useful discussions; particular mention should be made of George Rowlands.

I gratefully acknowledge the financial support made avaliable to me by the Science and Engineering Research Council through a post-graduate Research Associateship.

I thank the members of the Theoretical Physics Institute at the University of Marburg, West Germany, for their hospitality during my vist there in the summer of 1981. In particular I am grateful to Bijan Movaghar and Bernd Pohlmann for many interesting discussions.

Finally, and on a personal note, I thank Jenny and Debbie for all they have meant to me over the past three years.

DECLARATION

Except where indictated, the work reported in this thesis is the result of my own ~~independent~~ independent research. No details of this work have appeared in any thesis or dissertation at this, or any other, institution. Various aspects of the research reported herein have been published:

"The Percolation Threshold of a Diminishing Cayley Tree and its Relation to Hopping Conductivity" S.Summerfield and P.N. Butcher J. Phys. C Vol. 14 L585-7.

"Effective Medium Theory of A.C. Hopping Conductivity for Random-Bond Lattice Models" S.Summerfield Solid State Comm. Vol. 39 401-402.

"A Simple Extension of the Pair Approximation to A.C. Hopping Conductivity of a Disordered System to embrace the D.C. Limit" P.N.Butcher and S.Summerfield J. Phys. C Vol. 14 L1099-1102.

"A Unified Equivalent Circuit Approach to the Theory of A.C. and D.C. Hopping Conductivity in Disordered Systems" S.Summerfield and P.N.Butcher accepted for publication in J. Phys. C.

"Analysis of A.C. and D.C. Hopping Conductivity in Impurity Bands and Amorphous Semiconductors" S.Summerfield and P.N. Butcher accepted for publication in J. Phys. C.

Abstract

The theory of electron transport via hopping between localised states is developed within the framework of the rate equation approach and in particular the a.c and d.c. conductivity and Hall mobility are considered. The existence of substantial experimental data on the a.c. and d.c. conductivites motivates the development of a unified theory for these quantities. The availability of exact asymptotic conductivity formulae and computer generated data for a variety of special cases enables the validation of any particular approximation scheme prior to the analysis of experimental data. This in turn enables an unambiguous evaluation of the rate equation approach as a quantitative theory of transport in real systems.

The conductivity problem has two congruent representations; either a single particle random walk on a random lattice or an equivalent electrical circuit may be considered. In this work we examine both approaches and compare and contrast the methods used. Previous unified theories were exclusively based on the random walk approach and methods for evaluating the associated average Green's function; these methods are critically reviewed and extended. The equivalent circuit approach is then examined and a new theory is formulated which is simple to develop and yields improved results which agree well with asymptotic formulae and computer simulation data. Experimental data on a variety of systems is analysed; the extent of agreement obtained depends on the type of system considered and in some situations good agreement is found. Various problems are isolated which relate to the application of the rate equation model rather than the approximations used.

Finally the hopping Hall effect is considered. The lack of any reliable experimental data reduces the interest in the phenomenological aspect of the problem. However there exists computer simulation data; the utility and simplicity of the equivalent circuit approach is further demonstrated by the derivation of a theory that agrees with this data.

CHAPTER 1 - INTRODUCTION

1.1 Thermally Assisted Hopping

The descripion of the properties of a system which is ordered at the microscopic level is simplified by the intrinsic symmetry. In particular, as a consequence of the Bloch theorem, electrons in a crystal have well defined $\underline{k}$-quantum numbers and conduction processes can be described by transitions in $\underline{k}$- space. In contrast to this when we consider a disordered system, such as an array of randomly located impurities in a crystal or an amporphous solid, this desciption is not available. The theory of disordered systems lacks such a unifying feature as Bloch's theorem provided for ordered systems. However it has been accepted that disordered systems share the common property that the low lying electronic states are localised in space. We shall consider two types of solid in which such states occur. The first type is a doped crystalline semiconductor where there are localised states, lying in energy below the conduction band minimum, associated with the randomly located donor atoms (we shall for simplicity discuss an n-type semiconductor; equivalent statements are true for p-type). The second type is an amorphous semiconductor; we are concerned with electrons in a random lattice. Anderson (1958) shows how localised states can arise as a consequence of randomness; Mott (1969) postulates the existence of a 'mobility edge' separating localised from extended states in the extrema of the conduction and valence bands in an amorphous semiconductor.

The desciption of the transport of electrons in localised states must neccessarily be radically different

from the description in band states; the mean electron velocity is zero. We are concerned with transitions in $\underline{r}$-space and we refer to one such transition as a "hop" and the phenomenon associated with many hops as "hopping transport". In general the states will have different energies so that, apart from optical transitions, the transport among them can only proceed via an electron-phonon interaction. This concept of thermally assisted hopping forms the basis of the theory to be discussed below.

1.2 Impurity Conduction and the Rate Equation Model

Experimental observations on the low temperature electrical conductivity in doped crystalline semiconductors have implied that thermally assisted hopping can be the dominant transport mechanism. Mott and Twose (1961) review the early experimental data and discuss the preliminary theoretical analysis. For our purposes it is neccessary and sufficient to recall those features of the experimental data that motivate the need for a theory of hopping transport.

In following the behaviour of the d.c. electrical conductivity σ in a doped compensated crystalline semiconductor as liquid helium temperatures are approached, a marked change is apparent. At fairly low temperatures σ is due to activation of electrons from donor states to the conduction band and behaves as $\exp(-\beta\epsilon_1)$ where ϵ_1 is the activation energy related to the depression of the donor levels below the conduction band minimum. The dependence of σ on the density of donor states is fairly weak. At lower temperatures when this contribution to σ becomes small a

second contribution is observed. It is activated with a smaller activation energy and a change in the donor density of a factor of 10 can cause a change in σ of many orders of magnitude. This contribution is the impurity conduction due to hopping processes. This impurity conduction prevails as long as the donor density is small and we restrict our discussion to this case; at high densities a Mott transition takes place and the resulting impurity conduction is metallic- like due to the formation of extended states.

It has been observed more recently that at temperatures much lower than liquid helium the conductivity changes behaviour yet again to follow an $\exp(-[T_0/T]^{1/4})$ law, where T_0 is a characteristic temperature (Allen and Adkins 1974).

The first measurements of the a.c. impurity conduction were made by Pollak and Geballe (1961) who measured it in n- type silicon. They found a dependence on frequency ω of the real part of the a.c. conductivity $\sigma(\omega)$ proportional to ω^s with $s<1$. The temperature dependence of $\sigma(\omega)$ was found to be much weaker than the activated d.c. conductivity.

All the above features can be obtained from a model of thermally assisted hopping among singly occupied donor states. The restriction to single occupancy is implied by the absence of any measurable conductivity in uncompensated samples (Fritzsche 1958). The formulation of a complete quantitative theory is the semi- classical rate equation model of Miller and Abrahams (1960). Associated with each impurity state wave function is a site located at its centroid. The state of the whole system at time t is represented by a set of site occupation probabilities (f_m).

The probability f_m that a single electron occupies site m at time t satisfies

$$\frac{df_m}{dt} = \sum_n f_n(1 - f_m)R_{nm} - f_m(1 - f_n)R_{mn} \qquad (1.1)$$

The quantum mechanics of the system is subsumed into the transition rates $\{R_{mn}\}$. The equations were introduced phenomenologically; their intuitive appeal is obvious. They are analogous to the Boltzmann equation in band transport theory; one assumes a weak electron- phonon coupling so that the time spent by an electron in making a transition between localised states is negligible compared to the time spent in the states. The site occupation probabilities and transition rates are the counterparts of the $\underline{k}$- vector occupation numbers and scattering rates in Boltzmann transport theory. Despite this analogy and their relative success, the rate equations have been the centre of some controversy. Capek (1972, 1973, 1975) argues that they are an incorrect description of the system in the limit of weak electron- phonon coupling but Barker (1976) counters this by deriving them from the exact Kubo formula in this limit. It is beyond the scope of this work to engage in this discussion; we accept the rate equations as our starting point.

The statistical model assumptions are that the sites can be assigned independently distributed spatial co-ordinates and energies. The latter distribution will arise from the Coulomb field of the random array of charged acceptors. Together with the creation of vacancies among the donor states so that mobility is possible, this is the only role the acceptors play. The only electron- electron

correlation included relates to the restriction to single occupancy; the factors $((1-f_m))$ in equation (1.1) account for this. Spin dependent effects are neglected.

Miller and Abrahams calculate the transition rates in thermal equilibrium, R^0_{mn}, for an electron-phonon interaction of the deformation potential type between donor states in an n- type semiconductor. For the purposes of this work we accept a priori the validity of their results which may be summarised as

$$R^0_{mn} = R_0 \frac{\beta(\epsilon_1 - \epsilon_2)\ \exp(-2\alpha r_{mn} + \nu \ln \alpha r_{mn})}{\exp[\beta(\epsilon_1 - \epsilon_2)] - 1} \qquad (1.2)$$

with

$$R_0 = \frac{E_1^2 k_B T}{\pi \rho_0 V_s^5 \hbar^4} \left[\frac{e^2 \alpha}{6\pi\epsilon\epsilon_0}\right] \frac{1}{n_m} \left[\frac{\pi}{4\eta}\right]^{2-\nu}$$

where E_1, ρ_0, and V_s are the acoustic deformation potential, density and velocity of sound respctively. n_m is the number of conduction band minima and η is the ellipticity factor associated with impurity wave functions and is given by

$$\eta = \left[\frac{\alpha'^2}{\alpha^2} - 1\right]$$

where α and α' are the inverses of the major and minor impurity state Bohr radii respectively. The factor ν is associated with the structure of the conduction band minima and has the value 2 for spherical symmetry and 3/2 when the minima are strongly anisotropic. The last factor in R_0 is defined to be unity when $\nu = 2$. Simplified forms for R^0_{mn} will be used in this work from time to time in order to

demonstrate the main properties of the system.

1.3 Amorphous Semiconductors

Although formulated for impurity conduction, the rate equation model can be applied to a description of transport in amorphous semiconductors. This is motivated less by a confidence in their generality as by a lack of real theoretical progress in the realistic description of these undoubtably complex systems. Nevertheless the features of the experimental data are similar, the book of Mott and Davis (1979) contains a comprehensive review. The d.c. conductivity sometimes varies as the $T^{-1/4}$ law introduced above ; the first theoretical derivation of it from a hopping model is due to Mott (1969). The a.c. conductivity is again observed to behave as ω^s and has a weaker temperature dependence than the d.c. conductivity has. Activated d.c. conductivity is also observed .

1.4 A Survey of Previous Approaches and the Plan of this Thesis

The conductivity of the system governed by the equations (1.1) is obtained when they are linearised in the applied electric field; this is discussed in chapter 2.

It is clear from analyses prior to this work that the rate equation model can explain most of the qualitative features of the data on conduction in impurity bands and amorphous semiconductors (Butcher 1980). The most conclusive indication that this is indeed the case is provided by the invaluable direct numerical solutions of the linearised rate equations; the most comprehensive and accurate of these are

those performed by McInnes et. al. (Butcher, Hayden and McInnes 1977; Butcher and McInnes 1978; McInnes and Butcher 1979; McInnes, Butcher and Clark 1980; McInnes 1982). In the course of this thesis we make much use of these results and refer to them as "computer simulation data". The data identify the best simple analytic approximations. These are the percolation theory of d.c. conductivity (Ambegaokar et. al. 1971; Pollak 1972; Shklovskii 1973; Pike and Seager 1974), an approach based on the equivalent circuit analogy to be introduced in chapter 2, and the pair approximation to the a.c. conductivity (Pollak and Geballe 1961). The former approach is not immediately extendable to the a.c. case and the latter approach yields zero for $\sigma(0)$. It is therefore of theoretical and phenomenological interest to derive a unified theory for $\sigma(\omega)$, one which yields finite and accurate values for σ as $\omega \to 0$. The theoretical interest stems from the fact that we have a well defined random system for which we know absolute values of the electrical conductivity, for some special cases, from the computer simulations. This situation thus provides an invaluable testing ground for approximation methods in the theory of random systems. The phenomenological interest relates to the question of the validity of the rate equation model in the context of a consistent desciption of a.c. and d.c. conductivities, a question as yet unresolved.

The accuracy of a unified theory must be tested prior to the analysis of experimental data in order that an unambiguous evaluation of the rate equation model be made. Comparison with computer simulation data provides one test and the existence of asymptotic formulae provides another. These formulae are reviewed in chapter 3.

Previous unified theories have been formulated; they were based on the representation of the problem as a single particle random walk, a concept developed in chapter 2. The quantity of interest is an average Green's function; chapters 4 and 5 deal with methods for obtaining it. We present a systematic exposition of the various approximation schemes that have been used and examine their physical content and accuracy when compared to the asymptotic formulae. We make the extension to a unified theory of a method which has previously been used for the d.c. conductivity of a particular class of models. The most successful of the random walk approaches is the theory of Movaghar et. al. (1980 a,b,c; 1981); it is generally accurate but fails in some special cases upon comparison with computer simulation data and asymptotic formulae. In particular it does not reproduce the exactly known form of $\sigma(\omega)$ when the density of sites tend to zero at non-zero frequencies. It is also ~~complicated~~ complicated to derive and requires an intricate sequence of approximations. In order to seek an improved theory which is not excessively complicated, we consider a alternative approach based on the equivalent circuit representation introduced in chapter 2. In chapter 6 we use this approach to formulate an extended pair approximation to the conductivity. It is exceedingly simple to develop and represents a significant improvement over the results of the theory of Moveghar et. al. The final result reproduces all known asymptotic formulae in the appropriate limits and agrees well with the computer simulation data.

In chapter 7 we use the results of chapter 6 to analyse

a variety of experimental data. Our main observation therein is that a consistent description of a.c. and d.c. conductivity is only obtained when certain conditions prevail. One particular condition is a low carrier density. Various observations are made and some discrepencies uncovered; the possible extension of the rate equation theory to correct these is discussed as a topic for future research.

The Hall effect in a disordered hopping system is considered in chapter 8. The development of the relevent rate equations is reviewed; the basic process governing the response of the system is assumed to be the three- site mechanism proposed by Holstein (1961). There is little experimental evidence that the effect is in fact measurable (Amitay and Pollak 1966). However computer simulation data is available (Butcher and McInnes 1981; McInnes 1982); it is therefore a well- defined problem for which a suitably validated theory can await experimental confirmation. Such a theory is readily available via a simple extension of the methods used in chapter 6. We obtain a unified theory of a.c. and d.c. Hall mobility that agrees well with the computer simulation data. A comparison is made with the results of previous work in this area.

CHAPTER 2 - FORMAL EVALUATION OF THE A.C. CONDUCTIVITY: THE RANDOM WALK AND EQUIVALENT CIRCUIT REPRESENTATIONS

2.1 The Linearised Rate Equations

In this chapter we show how the a.c. conductivity may be evaluated for a system of electrons whose motion is determined by the rate equations introduced in the previous chapter. In this section we linearise the equations; the following two sections deal with the formal solutions in terms of the Green's function for an effective single-particle random walk, and in terms of the voltage differences arising in an equivalent electrical circuit.

We follow the formalism of Butcher (1976). In thermal equilibrium at temperature T the conventional procedures of statistical mechanics readily yield the solutions of the rate equations (1.1). They are the Fermi-Dirac functions

$$f_m = (\exp[\beta(\epsilon_m - \mu^*)] + 1)^{-1} \qquad (2.1.1)$$

where ϵ_m is the energy of an electron on site m and $\beta = (k_B T)^{-1}$. The quantity μ^* is $\mu + k_B T \ln 2$, where μ is the chemical potential. The $k_B T \ln 2$ term arises from the spin degeneracy associated with the states (Blakemore 1967) and is of little significance in a discussion of the conductivity. It can however become important when thermoelectric effects are considered (Aldea et. al. 1976). At T=0 μ^* is the Fermi level of the system and we shall, for the sake of economy of expression, refer to it as such at finite T, in keeping with terminology prevalent in the literature.

The principle of detailed balance requires that, in

thermal equilibrium, each term on the right hand side of the rate equations (1.1) vanishes individually. It therefore follows that the equilibrium transition rates R^0_{mn} satisfy

$$\frac{R^0_{mn}}{R^0_{nm}} = \exp[\beta(\epsilon_m - \epsilon_n)] \qquad (2.1.2)$$

Now suppose that a weak electric field $U(\underline{r},t)$ is applied to the system so that the potential at site m with position vector $\underline{r}_m$ is $U_m = U(\underline{r}_m,t)$. We approximate the effect of the applied potential on the transition rates by a shift in the energy at site m of U_m. The ratio R_{mn}/R_{nm} is then given by eqn. (2.1.2) with $\epsilon_m - \epsilon_n$ replaced by $(\epsilon_m + U_m) - (\epsilon_n + U_m)$ and to first order in U we obtain

$$\frac{R_{mn}}{R_{nm}} = [R^0_{mn}/R^0_{nm}][1+\beta(U_m - U_n)] \qquad (2.1.3)$$

The effect of the applied potential on this ratio is all that is required to solve the rate equations to first order. Equation (2.1.3) is valid in the static limit, neglecting the local field corrections which arise from the non-uniform distribution of charged electrons; an approximation valid when the carrier density is small.

In the presence of the applied potential f_m suffers a perturbation f^1_m. By substituting $f_m = f^0_m + f^1_m$ in eqn. (1.1) and using eqn. (2.1.2), we find that f^1_m is given to first order by the linearized rate equations

$$\frac{df_m}{dt} = \sum_n [f^1_n R^e_{nm} - f^1_m R^e_{mn}] + \beta \sum_n [F_n U_n R^e_{nm} - F_m U_m R^e_{mn}] \qquad (2.1.4)$$

where

$$R^e_{mn} = \Gamma_{mn}/F_m \qquad (2.1.5)$$

with $$\Gamma_{mn} = f_m^0(1 - f_n^0)R_{mn}^0 \qquad (2.1.6)$$

and $$F_m = f_m^0(1 - f_m^0)$$

$$= -k_B T df_m^0/d\epsilon_m \qquad (2.1.7)$$

We note here that Γ_{mn}, which is the electron flux from m to n in thermal equilibrium, is symmetrical in m and n because of detailed balance.

The formal solution of of eqns.(2.1.4) is facilitated by the introduction of matrix notation. We write $\underline{f}^1$ and $\underline{U}$ for row matrices whose mth columns are f_m^1 and U_m respectively and define a diagonal square matrix F whose (mm)th element is F_m. Finally, we define a relaxation matrix R whose (mn)th element is given by

$$R_{mn} = R_m^e \delta_{mn} - R_{mn}^e \qquad (2.1.8)$$

where $$R_m^e = \sum_n R_{mn}^e \qquad (2.1.9)$$

In general R_{mn}^e vanishes when m = n and where it does not, as in some artificial models, it will be implicit that its definition includes this property. With this notation, δ_{mn} representing the usual Kronecker δ-symbol, eqns. (2.1.4) become

$$\frac{d\underline{f}^1}{dt} = -\underline{f}^1 R - \beta \underline{U} F R \qquad (2.1.10)$$

2.2 Formal Solution in terms of the Effective Random Walk

In order to derive an expression for the ac conductivity at frequency ω, we suppose that $U(\underline{r},t)$ is the potential due to a uniform electric field E applied in the x-direction and having a sinusoidal time factor $\exp[-i\omega t]$. All the systems we consider are isotropic and the direction of the x-axis is arbitrary. Then $U(\underline{r},t) = eEx \exp[-i\omega t]$ and $\underline{U} = eE\underline{x} \exp[-i\omega t]$ where $\underline{x}$ is a row matrix whose mth column is x_m. Moreover $\underline{f}(t) = \underline{f}(0) \exp[-i\omega t]$ and eqn. (2.1.10) reduces to

$$\underline{f}^1(0)(R - i\omega) = -\beta eE\underline{x}FR \qquad (2.2.1)$$

The formal solution of eqn. (2.2.1) is

$$\underline{f}^1(0) = -\beta eE\underline{x}FRG \qquad (2.2.2)$$

where the Green's matrix G is defined by

$$(R - i\omega)G = 1 \qquad (2.2.3)$$

The induced dipole moment in the x-direction is

$$P_x(t) = -e\ \Omega^{-1}\underline{f}^1(t)\tilde{\underline{x}} \qquad (2.2.4)$$

where the tilde denotes the transpose of a matrix. The x-component of the current density is $-i\omega P_x(t)$ and the conductivity at frequency ω is therefore

$$\sigma(\omega) = \frac{-i\omega P_x(t)}{E \exp[-i\omega t]}$$

$$= -i\omega e^2\beta\ \Omega^{-1}\ \underline{x}FRG\tilde{\underline{x}} \qquad (2.2.5)$$

The matrix G defined by eqn.(2.2.3) has a simple stochastic interpretation. Consider the linearized rate equations (2.1.4) with E=0 and subject to the initial condition $f_m(o)= \delta_{mp}$. It is clear that they now represent the motion of a single random walker over the sites in the system, controlled by the effective transition rates R^e_{mn}; $f_m(t)$ is the probability of finding that particle at site m at time t which was initially created at site p at time t=0. Thus it becomes apparent that G_{mn} is the causal, or one-sided, Fourier transform of the probability of finding the particle at site n at time t if it was initially created at site m. With this observation it is now constructive to put eqn. (2.2.5) in another form. Because G_{mn} is the Fourier transform of a probability distibution it must obey the sum rule

$$\sum_n G_{mn} = \frac{-1}{i\omega} \tag{2.2.6}$$

This result, together with the definition of G and the symmetry of Γ_{mn} leads to the relations

$$RG = 1 + i\omega G \tag{2.2.7}$$

$$1 + i\omega G_{mm} = -i\omega \sum_{m\neq n} G_{mn} \tag{2.2.8}$$

$$F_m G_{mn} = F_n G_{nm} \tag{2.2.9}$$

We may thus eliminate the diagonal elements of G from eqn. (2.2.5) when the matrix products are written out in full. We then obtain

$$\sigma(\omega) = \omega^2 e^2 \beta\, \Omega^{-1} \sum_{mn}\sum F_m G_{mn} x_m (x_n - x_m) \tag{2.2.10}$$

The algebra is completed by symmetrising the summand in eqn. (2.2.10) and using eqn. (2.2.9). The final result is

$$\sigma(\omega) = -\frac{1}{2}\omega^2 e^2 \beta\, \Omega^{-1} \sum_{mn}\sum F_m G_{mn} (x_m - x_n)^2 \qquad (2.2.11)$$

The interpretation of eqn. (2.2.11) in terms of the single particle random walk becomes obvious when we remember that the electron density is

$$n = \Omega^{-1} \sum_m f_m^0 \qquad (2.2.12)$$

so that, using eqns. (2.1.1) and (2.1.7), we have

$$\frac{dn}{d\mu} = \beta\, \Omega^{-1} \sum_m F_m \qquad (2.2.13)$$

We may therefore rewrite eqn. (2.2.11) as

$$\sigma(\omega) = e^2 \frac{dn}{d\mu} D(\omega) \qquad (2.2.14)$$

where

$$D(\omega) = -\frac{1}{2}\omega^2 \left(\sum_m F_m\right)^{-1} \sum_m F_m \Delta_m^2(\omega) \qquad (2.2.15)$$

with

$$\Delta_m^2(\omega) = \sum_n G_{mn} (x_m - x_n)^2 \qquad (2.2.16)$$

Equation (2.2.14) has the form of a generalized Einstein relation at frequency ω for a degenerate electron system. The quantity $D(\omega)$ is identified as the diffusivity at frequency ω: $\Delta_m^2(\omega)$ is the causal Fourier transform of the mean square x-displacement at time t for the effective single particle setting out from site m at t=0. The summation in eqn. (2.2.15), with the factor F_m averages $\Delta_m^2(\omega)$ over all possible

initial states.

Scher and Lax (1973) derive eqns. (2.2.14) to (2.2.16) from a Kubo formula in the non- degenerate case. We note that our derivation does not rely on postulating the existence of the generalized Einstein relation; eqn. (2.2.14) arises naturally from the way we have linearised the equations.

When the system is sufficiently large, i.e. approaching the thermodynamic limit $N \to \infty$, $\Omega \to \infty$, $n_s = N/\Omega$ fixed, $\sigma(\omega)$ is accurately given by its configuration average, $\langle\sigma(\omega)\rangle$. We shall make explicit now the statistical assumptions that we shall be using throughout this thesis. We assume that the sites are distributed randomly and uniformly throughout the volume Ω and that the distribution of the site energies is given by $n_s^{-1}\rho(\epsilon)$, where $\rho(\epsilon)$ is the single-particle density of states for the localised electrons. With these assumptions we have, in d spatial dimensions

$$\langle\sigma(\omega)\rangle = -\frac{1}{2d}\,\omega^2 e^2 \beta \int d\epsilon_m \rho(\epsilon_m) \int d\epsilon_n \rho(\epsilon_n) \int dr_{mn}\, \pi (2r_{mn})^{d-1} \ldots\ldots$$

$$\ldots\ldots (r_{mn})^2\, F(\epsilon_m) \langle G(r_{mn}, \epsilon_m, \epsilon_n; \omega)\rangle' \qquad (2.2.17)$$

The quantity $\langle G(r_{mn}, \epsilon_m, \epsilon_n; \omega)\rangle'$ is the off-diagonal Green's matrix element G_{mn} averaged over all site variables in the system except the site energies ϵ_m and ϵ_n and r_{mn}; chapters 4 and 5 are concerned with approximations to this function.

2.3 Formal Solution in Terms of the Equivalent Circuit

By changing notation we can show that the problem has an equivalent RC network; hitherto unforseen possibilities for physical intuition as a guide to mathematical approximation

therefore emerge.

Consider the linearised rate equations (2.1.10). If we put $f_m^1 = \beta F_m \Phi_m$ and $V_m = -(\Phi_m + U_m)e^{-1}$ and multiply both sides by -e, they become

$$C_m \frac{d}{dt}\left[V_m + e^{-1}U_m\right] = -\sum_n g_{mn}(V_m - V_n) \qquad (2.3.1)$$

where

$$g_{mn} = e^2\beta\,\Gamma_{mn} \qquad (2.3.2)$$

and

$$C_m = e^2\beta\,F_m \qquad (2.3.3)$$

Now consider an elecrical network having nodes that coincide with the electron sites. Suppose that each node is connected to ground by a series combination of a voltage generator $-e^{-1}U_m$ and a capacitance C_m and suppose that a conductance g_{mn} connects nodes m and n. Writing V_m for the voltage at node m we find that application of Kirchoff's first law to this circuit leads to precisely equations (2.3.1). This equivalent circuit is shown in Figure 1. It is now perfectly straightforward to determine $\sigma(\omega)$ in terms of the (V_m). The left hand side of eqn. (2.3.1) is $-e\,df_m^1/dt$ so that using eqn. (2.2.4) and assuming $V_m = V_m(0)\exp(-i\omega t)$, we obtain

$$\sigma(\omega) = -\frac{1}{2\Omega E}\sum_{mn}\sum g_{mn}V_{mn}x_{mn} \qquad (2.3.4)$$

where $V_{mn} = V_m - V_n$ and $x_{mn} = x_m - x_n$. An alternative formula exists for $\sigma_1(\omega)$, the real part of $\sigma(\omega)$ and can be obtained by algebraic manipulation of eqn. (2.3.4) or by equating the Joule heating in the volume to the sum of powers dissipated in the individual conductances:

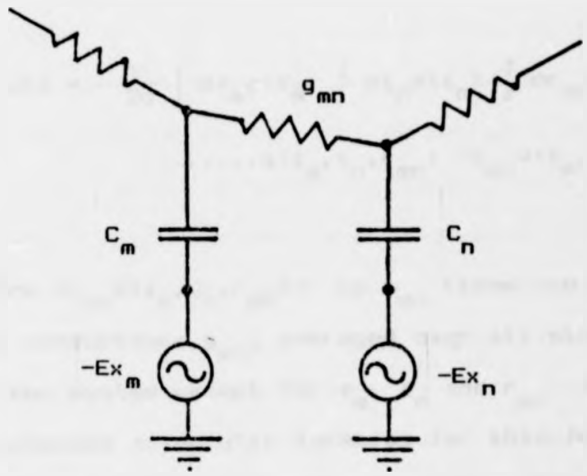


FIGURE 1

Two nodes in the equivalent circuit

$$\sigma_1(\omega) = \frac{1}{2\Omega E} \sum_{mn}\sum g_{mn}|V_{mn}|^2 \qquad (2.3.5)$$

Calculation of the configuration average proceeds in exactly the same way as in the previous section and, for example, we have from (2.3.4)

$$\langle\sigma(\omega)\rangle = -\frac{1}{2d}\int d\epsilon_m \rho(\epsilon_m)\int d\epsilon_n \rho(\epsilon_n)\int dr_{mn}\pi(2r_{mn})^{d-1}\ldots\ldots$$

$$\ldots\ldots\ldots g(\epsilon_m,\epsilon_n,r_{mn})\,\langle x_{mn}V(\epsilon_m,\epsilon_n,r_{mn})\rangle' \qquad (2.3.6)$$

where $\langle x_{mn}V(\epsilon_m,\epsilon_n,r_{mn})\rangle'$ is x_{mn} times the voltage drop across the conductance g_{mn}, averaged over all stochastic variables in the system except for ϵ_m, ϵ_n and r_{mn}. In the next chapter we discuss asymptotic formulae for this function and in chapter 6 we find a unified approximation to it.

CHAPTER 3 - ASYMPTOTIC CONDUCTIVITY FORMULAE

3.1 Introduction

In certain regions of the system parameter space there is precise information available on the conductivity. Exact formulae are available for $\sigma(\omega)$ when the frequency $\omega \to \infty$ and, in the limit $T \to \infty$, when the site density n_s is very large. When n_s tends to zero and ω is non zero $\sigma(\omega)$ has an expansion in powers of n_s (Butcher and Morys 1973). The leading term is the pair approximation to $\sigma(\omega)$ (Pollak and Geballe 1961) which is therefore exact as $n_s \to 0$. Percolation theory (ops. cit. chapter 1) provides much information on the d.c. conductivity in the low density limit. The results that can be obtained are reviewed in detail in the remaining sections of this chapter as, together with the numerical solutions of the rate equation (ops. cit. chapter 1), they provide the means of assessing the accuracy of approximations to $\sigma(\omega)$ prior to the analysis of experimental data.

3.2 The High Frequency and High Density Limits

The random walk or equivalent circuit notations can be used with equal success to discuss these limits. For simplicity of development we prefer here to use the latter approach. Consider first the limit $\omega \to \infty$; inspection of eqns. (2.3.1) immediately yields

$$V_{mn} = - E x_{mn} \quad \text{as} \quad \omega \to \infty \qquad (3.2.1)$$

Upon averaging over all possible orientations of the vector x_{mn} in d dimensions,

$$\langle x_{mn} V_{mn} \rangle' = - E r_{mn}^2 / d \qquad (3.2.2)$$

is obtained and substitution into eqn. (2.3.6) gives

$$\sigma(\omega) = \frac{1}{2d} \int \rho(\epsilon_m) d\epsilon_m \int \rho(\epsilon_n) d\epsilon_n \int dr_{mn} \pi r_{mn}^2 (2r_{mn})^{d-1} g(\epsilon_m, \epsilon_n, r_{mn}) \qquad (3.2.3)$$

In the limit $T \to \infty$ the energy dependent factors in the transition rates vanish and the equilibrium site occupation probabilities reduce to n/n_s. $\langle x_{mn} V_{mn} \rangle'$ is therefore independent of ϵ_m and ϵ_n and all the randomness of the system is contained in the fluctuations of intersite separations. These fluctuations vanish as $n_s \to \infty$ as does the right hand side of eqns. (2.3.1) by virtue of the resulting inversion symmetry. Hence V_{mn} is again given by eqn. (3.2.1) so that

$$\sigma(\omega) = \frac{n_s^2}{2d} \int dr_{mn} \pi r_{mn}^2 (2r_{mn})^{d-1} g(r_{mn}) \qquad \text{as } n_s \to \infty \qquad (3.2.4)$$

which is independent of ω.

These formulae have little relevence in the analysis of experimental data. In the former case the whole procedure of chapter 2 breaks down with the onset of transitions involving direct photon absorption. In the high density limit localization is no longer expected and the rate equation model itself is not applicable. However well-defined results are available for these cases in the computer simulation data and thus they still have a role to play in the validation of approximations to $\sigma(\omega)$.

3.3 The Low Density Limit at Finite ω: The Pair Approximation

The pair approximation has a venerable history as a simple a.c. conductivity formula. It is successful in that it gives the ω^s form of $\sigma(\omega)$ observed experimentally and compares quite favourably with computer simulation data (McInnes, Butcher and Clark 1980). It has been used extensively in the analysis of experimental data on impurity conduction (Pollak and Geballe 1961, Golin 1963) and conduction in amorphous semiconductors (e.g. Mott and Davis 1979). Pollak and Geballe derive it as a model for the a.c. impurity conduction in doped silicon under conditions of low compensation. The acceptors are then considered as effectively isolated and, since the ionised donors are expected to be in their vicinity, the conducting regions are isolated too. Each isolated region is represented by a pair of sites between which one electron can execute reciprocating hops. This concept has an intuitive appeal for highly random (low density) systems in that at very high frequencies the resonant modes of the system are dominated by hopping between anomalously close pairs of sites. In fact Butcher and Morys (1973) were able to show that the pair approximation is the leading term in the expansion of $\sigma(\omega)$ in powers of the site density. Their proof is restricted to non-zero frequency as it is based on selecting terms in the expansion of the Greens function in powers of $1/\omega$. The model of isolated conducting regions is at variance with the data in that there is an experimentally observed d.c. conductivity for which the prediction of the pair approximation is zero.

We shall now derive the pair approximation by considering the linearised rate equations (2.3.1) for an

isolated pair of sites, labelled 1 and 2. Our treatment differs from that of Pollak and Geballe in terms of statistical assumptions; in assuming the pairs to be truly isolated they set the total occupancy of each of those pairs to unity. This procedure is incorrect in so far as the pairs are not truly isolated. The accuracy of the approximation in the low density limit relates to motion on a finite time scale since we consider non-zero frequency. The establishment of thermal equilibrium over the whole system must be allowed infinite time; the interaction between the pairs, which is negligible on a finite time scale, ensures that the equilibrium occupation probabilities are given by the Fermi-Dirac functions eqn.(2.1.1). The equations for the voltages on an isolated pair of sites are thus

$$-i\omega C_1(V_1 + Ex_1) = - g_{12}V_{12} \qquad (3.3.1a)$$

$$-i\omega C_2(V_2 + Ex_2) = g_{12}V_{12} \qquad (3.3.1b)$$

so that

$$V_{12} = - \frac{Ex_{12}}{Z_p g_{12}} \qquad (3.3.2)$$

where

$$Z_p = \frac{1}{g_{12}} - \frac{1}{i\omega C_1} - \frac{1}{i\omega C_2} \qquad (3.3.3)$$

The resulting formula for $\sigma(\omega)$ is obtained upon sustitution of eqn. (3.3.2) into eqn (2.3.6).

The role of temperature in this analysis is that of a density reduction factor. At high temperatures the accuracy of the pair approximation is determined by the value of n_s

(on the length scale defined by α). At low temperatures the exponential dependence in the equilibrum site occupation probabilities effectively isolates sites far away from the fermi level.

3.4 The Low Density Limit at Zero Frequency: Percolation Theory

3.4.1 The Assertion of Percolation Theory

When $\omega = 0$ there is no exact expression available for $\sigma(\omega)$ but the idea that percolation theory can determine the main dependences of $\sigma(0)$ is well established (Ambegaoker et.al. 1971, Pollak 1972, Shklovskii 1973, Pike and Seager 1974) and is confirmed by detailed comparison with computer simulation and experimental data (Butcher, Hayden and McInnes 1977, Hayden and Butcher 1978, Butcher 1980). Its application requires that fluctuations in the hopping rates become large; it is therefore a low density or low temperature approximation. The exponential dependences in the rates explain its success well away from the truly asymptotic region.

Let us write the conductances eqn.(2.3.2) in the form

$$g_{mn} = g_0 \exp(-s)$$

where with the eqn. (1.2) for the (R_{mn}), for example, s is given by

$$s = 2\alpha r + v\ln\alpha r + \ln[8\cosh(\beta\epsilon_1/2)\cosh(\beta\epsilon_2/2)\sinh(\beta[\epsilon_1 - \epsilon_2]/2)] - \ln[\beta(\epsilon_1 - \epsilon_2)] \qquad (3.4.1)$$

and where $g_0 = e^2 \beta R_0$

Percolation theory asserts that the conductivity contains the factor $\exp(-s_p)$, where s_p is the critical value of s in an associated percolation problem. This is defined as follows. A large value of s, s_0 say, is chosen and conductances with $s>s_0$ are removed from the system. This procedure is repeated with s_0 being reduced continuously until the network just fails to conduct at all. The value of s_0 at which this happens is called s_p; it is the critical value of s_0 for the formation of an infinite connected cluster.

The foundation of the assertion, based on an intuitive reasoning of the current distribution in the conductances, is discussed at length by Hayden (1978). It is supposed that as s is decreasing the current flow through some conductance g_{mn} increases until it rapidly saturates when $s = s_p$. The power dissipated in g_{mn} has therefore a sharp peak at $s = s_p$ and this fact motivates a simple ansatz for $\langle |V_{mn}|^2 \rangle'_{\delta}$,used in eqn. (2.3.4), which is subsequently found to be surpisingly accurate (Butcher, Hayden and McInnes 1979).

It is reasonable to expect some form of current limiting to take place as the current flowing in an anomalously large conductance will be primarily determined by the current fed into it from the surrounding network. The identification of s_p with the current-limiting value of s has intuitive appeal but has yet to be rigorously demonstrated. Nevertheless the predictions which percolation theory makes are quite precise and fully consistent with the available data. For the purposes of this work it is useful to understand the physical process that affects the current limiting in the random walk picture. The d.c. conductivity is determined by the most

favourable paths available to the particle that extend throughout the whole system. It is clear that the effect of an anomalously large hopping rate will not be to enhance the the progress of the particle along these paths. If sites m and n are connected by such a rate then, were the particle to hop from site m to site n, the most likely hop to follow would be a return to site m. The relationship of this correlated back-hopping to the intuitively expected current limiting is of consequence in the approximations to the conductivity based on the random walk picture that we shall discuss in chapters 4 and 5.

Various hopping models are defined by the choice of v in eqn.(3.4.1), the form of the density of states or the limit $T \to \infty$. The energy dependence in s is sometimes replaced by a simplified form. Some of the associated percolation problems have been studied and we shall look at those which relate to d.c. conductivities that have been calculated by computer simulation.

3.4.2 R-Hopping in d Dimensions

The R-hopping model arises either in the limit $T \to \infty$ or with the density of states

$$\rho(\epsilon) = n_s \delta(\epsilon) \qquad (3.4.2)$$

The result in either case is an energy independent model with

$$s = 2\alpha r_{mn} + v \ln \alpha r_{mn} \qquad (3.4.3)$$

where any constant factor remaining in s is absorbed into the

definition of g_0. We consider the case $\nu = 0$. The associated percolation problem invovles the formation of an infinite connected cluster of randomly located d-dimensional spheres of radius s_0; it has been studied via direct computer simulation by Pike and Seager (1974). Their results can be summarised as

$$s_p = \left[\frac{6N_p^{(3)}\alpha^3}{m_s} \right]^{1/3} \qquad (3.4.4a)$$

in three dimensions and

$$s_p = \left[\frac{4N_p^{(2)}\alpha^2}{m_s} \right]^{1/2} \qquad (3.4.4b)$$

in two dimensions, where N_p is the number of bonds per site at the percolation threshold with $N_p^{(3)} \cong 2.7$ and $N_p^{(2)} \cong 4.5$.

3.4.3 Energy Dependent Model in Three Dimensions

we shall consider a model where

$$\begin{aligned} \rho(\epsilon) &= n_s/W && |\epsilon| < W/2 \\ &= 0 && \text{otherwise} \end{aligned} \qquad (3.4.5)$$

and s takes on the simplified form due to Ambegaoker et. al.(1971); it is an approximation to equation (3.4.1) with $\nu = 0$ which is useful for $\beta\epsilon >> 1$. We have

$$s = 2\alpha r_{mn} + \beta(|\epsilon_m| + |\epsilon_n| + |\epsilon_m - \epsilon_n|)/2 \qquad (3.4.6)$$

Unfortunately there have been no direct computer simulations of the associated percolation problem for this case. However,

when T is small it may be permissible to treat the energy as an effective fourth dimension. For four dimensional hyperspheres Pike and Seager find $N_p^{(4)} \cong 2.1$. With s as given above we are strictly speaking not concerned with the percolation of hyperspheres. Nevertheless Butcher and Hayden (1977) equate an appropriate number of bonds per site to $N_p^{(4)}$ and find

$$s_p = \left[\frac{40 N_p^{(4)} \alpha^3}{n\rho(\mu^*) k_B T} \right]^{1/4} \qquad (3.4.7)$$

where μ^* is the fermi level.

3.4.4 Analytic Calculation of s_p

A theory of d.c. hopping conductivity is also a theory of the percolation problem. The percolation threshold is determined by replacing the $\langle g_{mn} \rangle$ with the step conductances

$$\begin{aligned} g_{mn} &= g_0 \qquad s \leq s_0 \\ &= 0 \qquad s > s_0 \end{aligned} \qquad (3.4.5)$$

The value of s_p is then the value of s_0 for which $\sigma(0)$ just vanishes. This observation will be used in subsequent work to investigate the consistency of any particular approximation with the predictions of percolation theory and to allow correction factors to be introduced where neccessary.

CHAPTER 4 - UNIFIED THEORY BASED ON THE RANDOM WALK APPROACH 1: DECOUPLING AND SELF-CONSISTENT APPROXIMATIONS TO THE GREEN'S FUNCTION

4.1 Introduction

This chapter and the next are concerned with the investigation of methods of approximating the average Green's function introduced in section 2.2. This chapter deals with techniques for the direct averaging and summation of the Dyson expansion. Effective medium theory is discussed in chapter 5.

The methods considered in this chapter are developed for the R-hopping model introduced in section (3.4.2)., generalisation to the energy dependent case will be discussed later. For R-hopping the conductivity is given by

$$\sigma(\omega) = e^2\beta\, n(1 - n/n_s)\, D(\omega) \qquad (4.1.1)$$

where

$$D(\omega) = -\frac{1}{2N}\,\omega^2 \sum\sum_{mn} G_{mn}(x_m - x_n)^2 \qquad (4.1.2)$$

With the same statistical assumptions that led to eqn. (2.2.17), the configuration average of $D(\omega)$ is given by:

$$\langle D(\omega)\rangle = -\frac{1}{2d}\,\omega^2 n_s^2 \int dr_{mn}\, r_{mn}^2 (2r_{mn})^{d-1} \langle G(r_{mn};\omega)\rangle' \qquad (4.1.3)$$

The function $\langle G(r_{mn};\omega)\rangle'$ is the function defined in eqn. (2.2.17) with transition rates that depend only on inter-site separations; it is the off-diagonal matrix element G_{mn}, averaged over all configurations of the system with the distance r_{mn} held fixed. It is convenient to rewrite equation (4.1.3) in terms of the Fourier transformed

average Green's function, $\hat{G}_{\underline{k}}$, defined by

$$\hat{G}_{\underline{k}} = \int \exp(i\underline{k}.\underline{r}_{mn}) \langle G(r_{mn};\omega)\rangle' \, d\underline{r}_{mn} \qquad (4.1.4)$$

where $\underline{r}_{mn} = \underline{r}_m - \underline{r}_n$. We obtain directly

$$\langle D(\omega)\rangle = - \frac{\omega^2 n_s^2}{6} \nabla_{\underline{k}}^2 \hat{G}_{\underline{k}} \Big|_{\underline{k}=\underline{0}} \qquad (4.1.5)$$

The sum rule, eqn. (2.2.6), becomes in this notation

$$\langle G_{mm}\rangle + n_s \hat{G}_{\underline{0}} = \frac{-1}{i\omega} \qquad (4.1.6)$$

In order to derive approximations to $\hat{G}_{\underline{k}}$ we make use of the Dyson expansion of G. It is a particularly useful approach as each term can be shown to have a definite stochastic interpretation in terms of the effective single particle random walk. The interpretation of a particular approximation scheme as a set of physical assumptions concerning the random walk is then possible. Using eqn. (2.1.8) we can write eqn. (2.2.3) in the form

$$([G^0]^{-1} - R^1)G = 1 \qquad (4.1.7)$$

where

$$G^0_{mn} = \frac{\delta_{mn}}{R^e_m - i\omega} \qquad (4.1.8)$$

and

$$\begin{aligned} R^1_{mn} &= R^e_{mn} \qquad m \neq n \\ &= 0 \qquad\quad m = n \end{aligned} \qquad (4.1.9)$$

Upon iteration of eqn. (4.1.7) we obtain the Dyson expansion of G:

$$G = G^0 + G^0R^1G^0 + G^0R^1G^0R^1G^0 + \ldots\ldots \qquad (4.1.10)$$

whose matrix elements are given by

$$G_{mn} = G^{o}_{mm}\delta_{mn} + G^{o}_{mm}R_{mn}G^{o}_{nn} + \sum_{p} G^{o}_{mm}R_{mp}G^{o}_{pp}R_{pn}G^{o}_{nn} + \sum\sum_{pq}..... \qquad (4.1.11)$$

where we have, for ease of writing, dropped the superscript e on the $\{R_{mn}\}$.

The stochastic interpretation of eqn. (4.1.11) becomes obvious when we notice that the probability that an electron placed on site m at time zero will wait there without hopping away until time t is $\exp(-tR_m)$. The causal Fourier transform of this is just G^{o}_{mm}; the leading term in eqn. (4.1.11) with m = n. Furthermore, the probability that an electron will wait at site m until time τ, then make a single hop to site $n \neq m$ in the time interval $(\tau, \tau + d\tau)$ and finally wait on site n until time t is

$$\exp(-\tau R_m)R_{mn}d\tau \exp[-(t - \tau)R_n] \qquad (4.1.12)$$

Upon integrating this expression with respect to τ from 0 to t and taking the causal Fourier transform, we obtain the leading term in eqn. (4.1.11) with $n \neq m$. The higher order terms may be generated in a similar way. The Nth. term has an interpretation in terms of the electron created at site m at time zero being found at site n at time t having made N-1 hops to get there.

The problem of determining $\hat{G}_{\underline{k}}$ is now to average each term in (4.1.11) over all site locations except for $\underline{r}_m$ and $\underline{r}_n$, sum the series and take the Fourier transform defined in eqn. (4.1.4). The degree of correlation present in the system makes this intractable without some approximation.

If we allow only m and n themselves as intermediate sites the averaging is trivial and the series reduces to an infinite geometric progression. This defines the pair approximation in this notation (Butcher 1976) which yields zero for $\sigma(0)$. The same is true with any restriction of intermediate sites to a finite cluster whence G_{mn} will tend to a finite value as $\omega \to 0$; the factor ω^2 in eqn. (4.1.2) then ensures $\sigma(0) = 0$. In order to obtain a finite d.c. conductivity N sites must be included in the summation in the thermodynamic limit.

When considering the configuration average of eqn. (4.1.11) it is of note that two types of correlation arise. The $\langle G^0_{mm} \rangle$ are correlated to the $\langle R_{mn} \rangle$ via the relationship $R_m = \sum_n R_{mn}$; we shall refer to this as correlation of the first type. The definition of correlations of the second type will relate to the possibility of coincidence among the site indices in a term in the expansion. Terms in the expansion of G_{mn} can be classified according to the degree of correlation of the second type; a diagrammatic representation is possible but superfluous for our purposes. Some decoupling is required in practice; as the level of correlation included in an approximation increases so too does the level of mathematical sophistication required. Of interest to us in what follows is the ability of approximations at particular levels to reproduce, in the appropriate limits, the asymptotic formulae introduced in the previous chapter. Success is defined as the reproduction of all the information given there. The following sections show that limited success can follow from quite simple approaches. In section 4.2 we include only correlations of the first type in the averaging procedure and find that this

produces the kind of dispersive a.c. behaviour observed in computer simulations and experiment. The picture obtained for the d.c. conductivity is found to be incorrect in as much as being in variance with the predictions of percolation theory. The result will be interpreted in terms of the physical content of the approximation. We show in section 4.3 that extending the approximation by the inclusion of a self-consistent element, accounting too for some correlations of the second type, leads to agreement with the general predictions of percolation theory. Precise forms of the conductivity exponents are not however obtained. In section 4.4 we discuss the type of analysis that would be required to achieve this with the methods used in this chapter and conclude that it is not practical in view of the availability of the effective-medium method, discussed in chapter 5.

The remaining question concerning the effect of including some particular level of correlation in the Green's function average related to the neglect of correlations of the first type while accounting for correlations of the second type. This would naturally identify the hopping problem with the usual formulation of tight-binding theory in a random system (see e.g. Elliot, Krumhansl and Leath 1974). The independently distributed functions $R_m \neq \sum_n R_{mn}$ are then analogous to the site energies and the (R_{mn}) correspond to the transfer integrals. This approach would open up the possibility of using the extensive formalism already developed for the tight-binding problem. However we will show that neglecting correlations of the first type within the approach developed in section 4.3 leads to the result $D(\omega) = D(\infty)$.

Before discussing approximations based on including correlation of some type, let us briefly indicate the result obtained with none. This is the analogue of the Virtual Crystal Approximation in tight-binding theory. Equation (4.1.7) is re-written as

$$G = G^{0} + G^{0}R^{1}G \tag{4.1.13}$$

and the matrix elements of G_{mn} become

$$G_{mn} = G^{0}_{mm}\delta_{mn} + \sum_{p} G^{0}_{mm}R_{mp}G_{pn} \tag{4.1.14}$$

we now average over all site locations except for $\underline{r}_m$ and $\underline{r}_n$. Neglecting correlations of the first type implies the the replacement $G^{0}_{mm} = \langle G^{0}_{mm} \rangle = \gamma$, say and neglect of correlations of the second type leads us to exclude the terms in the summation in eqn. (4.1.14) with p = n and p = m. One then obtains for large N

$$\langle G_{mn} \rangle' = \gamma \left[\delta_{mn} + n_s \int d\underline{r}_p \, R_{mp} \langle G_{pn} \rangle' \right] \tag{4.1.15}$$

Now R_{mn} depends only on the site separation r_{mn} so that $\langle G_{mn} \rangle'$ will too, and the integral equation is of the convolution type. Therefore upon taking the Fourier transform defined in eqn. (4.1.4), it is found that

$$\hat{G}_{\underline{k}} = \gamma \left[1 + n_s \hat{R}_{\underline{k}} \hat{G}_{\underline{k}} \right] \tag{4.1.16}$$

where

$$\hat{R}_{\underline{k}} = \int \exp(i\underline{k}.\underline{r}_{mn}) \, R_{mn} d\underline{r}_{mn} \tag{4.1.17}$$

so that

$$\hat{G}_{\underline{k}} = \frac{\gamma}{1 - n_s \hat{R}_{\underline{k}} \gamma} \tag{4.1.18}$$

and finally

$$\nabla_{\underline{k}}^2 G_{\underline{k}}\big|_{\underline{k}=0} = \frac{n_s^2 \gamma^3 \nabla_{\underline{k}}^2 R_{\underline{k}}\big|_{\underline{k}=0}}{(1 - n_s \hat{R}_{\underline{0}} \gamma)^2} \tag{4.1.19}$$

is obtained where macroscopic isotropy leads to terms involving $\nabla_{\underline{k}} \hat{G}_{\underline{k}}\big|_{\underline{k}=\underline{0}}$ vanishing. Within the approximations that led to eqn. (4.1.15) $G_{mm} = G^0_{mm}$ so that, applying the sum rule, eqn. (4.1.6), we find that

$$1 - n_s \hat{R}_{\underline{0}} \gamma = i\omega n_s \gamma \tag{4.1.20}$$

and substitution of eqn. (4.1.19) into eqn. (4.1.5) yields.

$$\langle D(\omega) \rangle = \frac{n_s}{2d} \nabla_{\underline{k}}^2 R_{\underline{k}}\big|_{\underline{k}=0} = \langle D(\infty) \rangle \tag{4.1.21}$$

4.2 Pairwise Decoupling Approximation

We shall now develop the approximation to $\hat{G}_{\underline{k}}$ that results from including some of the correlation between the $\{R_m\}$ and the $\{R_{mn}\}$. The neglect of correlations involved in the possibilty of repeated indices in terms of the expansion of G_{mn} implies the selection of terms corresponding to a self-avoiding walk. The result is a simple convolution structure.

The method we employ is to consider only the correlation

between a particular G^0_{ii} in eqn. (4.1.11) and the preceeding hop rate. The physical content of this approximation will be discussed below. The average off-diagonal Green's matrix element is now given by

$$\langle G_{mn}\rangle' = \langle G^0_{mm}\rangle\left[\langle R_{mn}G^0_{nn}\rangle' + n_s\int d\underline{r}_p \langle R_{mp}G^0_{pp}\rangle'\langle R_{pn}G^0_{nn}\rangle' + \ldots\ldots\right] \tag{4.2.1}$$

Making the definitions

$$\gamma(\omega) = \langle G^0_{mm}\rangle \tag{4.2.2}$$

and

$$h(\omega, r_{mn}) = n_s\langle R_{mn}G^0_{nn}\rangle' \tag{4.2.3}$$

and taking the Fourier Transform of eqn.(4.2.1), we have

$$\hat{G}_{\underline{k}} = n_s^{-1}\gamma\left[\hat{h}_{\underline{k}} + \hat{h}^2_{\underline{k}} + \ldots\ldots\ldots\ldots\right]$$

$$= \frac{n_s^{-1}\gamma}{1 - \hat{h}_{\underline{k}}} - n_s^{-1}\gamma \tag{4.2.4}$$

where

$$\hat{h}_{\underline{k}} = n_s\int \exp(i\underline{k}.\underline{r}_{mn})h(\omega, r_{mn})d\underline{r}_{mn} \tag{4.2.5}$$

and thus

$$\langle D(\omega)\rangle = -\frac{1}{2d}\frac{\gamma\omega^2}{[1 - \hat{h}_{\underline{0}}]^2}\nabla^2_{\underline{k}}\hat{h}_{\underline{k}}\Big|_{\underline{k}=\underline{0}} \tag{4.2.6}$$

Now

$$\sum_n R_{mn}G^0_{nn} = \sum_n\left[1 + \frac{1}{\sum_p R_{np} - i\omega}\right] \tag{4.2.7}$$

so that upon averaging this we find that

$$\hat{h}_{\underline{0}} = 1 + i\omega\gamma(\omega) \qquad (4.2.8)$$

and finally obtain

$$\langle D(\omega)\rangle = \frac{1}{2d\gamma(\omega)} \int h(\omega, r_{mn})\, r_{mn}^2\, d\underline{r}_{mn} \qquad (4.2.9)$$

Upon writing writing eqn. (4.2.9)in the form

$$\langle D(\omega)\rangle = \frac{1}{2d} \langle r^2(\omega)\rangle \left[\frac{1}{\gamma(\omega)} - i\omega \right] \qquad (4.2.10)$$

where

$$\langle r^2(\omega)\rangle = \hat{h}_{\underline{0}}^{-1} \nabla_{\underline{k}}^2 \hat{h}_{\underline{k}} \Big|_{\underline{k}=\underline{0}} \qquad (4.2.11)$$

we immediately recognise the final result of the continuous time random walk theory of Scher and Lax (1973), derived in a somewhat different way, providing that $\langle r^2(\omega)\rangle$ is replaced by $\langle r^2(0)\rangle$. McInnes, Butcher and Clark (1980) make a comparison of this theory with computer simulation data; the theory correctly reproduces the low and intermediate frequency a.c. behaviour of the data but shows some error in the d.c. limit and at high frequencies.

Let us investigate the ~~accurracy~~ accuracy of the result in the asymptotic limits discussed in chapter 3. When $\omega \to \infty$, $\gamma \to -1/i\omega$ and $h \sim -R_{mn}/i\omega$; upon comparison with eqn. (3.2.3) it is easily seen that the theory is exact in this limit. The final result of Scher and Lax is not, since $\langle r^2(\infty)\rangle$ is not equal to $\langle r^2(0)\rangle$. It is not difficult to see that the correct high density limit is also obtained. In the low density limit at finite frequency, selecting the leading term in eqn (4.2.1) leads to

$$\langle G_{mn}\rangle' \sim \langle G^0_{mm}\rangle \langle R_{mn} G^0_{nn}\rangle' \quad \text{as } n_s \to 0$$

$$= \left\langle \frac{1}{R_{mn} - i\omega} \right\rangle \left\langle \frac{R_{mn}}{R_{mn} - i\omega} \right\rangle' \qquad (4.2.11)$$

Butcher writes down the exact Green's function for this case, the pair approximation, and finds

$$\langle G_{mn} \rangle' = \frac{R_{mn}}{-\omega^2 + 2i\omega R_{mn}} \qquad (4.2.12)$$

Substitution of this result into eqn. (4.1.2) gives the same formula for $\sigma(\omega)$ as does substitution of eqn. (3.3.2), with $C_1 = C_2$, which is appropriate for the limit $T \to \infty$, into eqn. (2.3.4). The differences between eqn. (4.2.11) and eqn. (4.2.12) reflect the way that averages are factored. In view of this it is surprising that the Scher and Lax theory should be in such good agreement with the computer data.

Butcher (1974) has calculated the low density d.c. conductivity predicted by eqn. (4.2.10) by assuming that the nearest neighbour is the site to which the particle will always hop. Using

$$R_{mn} = R_0 \exp(-2\alpha r_{mn}) \qquad (4.2.13)$$

he finds, in three dimensions

$$h(\omega, r_{mn}) = \frac{R_0 \exp(-2\alpha r_{mn})\, n_s \exp(-\frac{4}{3}\pi n_s r_{mn}^3)}{R_0 \exp(-2\alpha r_{mn}) - i\omega} \qquad (4.2.14)$$

where the additional exponential factor in the numerator is the probablility of finding the nearest neighbour to site m a distance r_{mn} away. With this form it readily follows that the d.c. conductivity contains the factor $\exp(-an_s^{-2/3})$, where a is a constant. Recalling that percolation theory

predicts a factor of the form $\exp(-an_s^{-1/3})$, we immediately see a qualitative discrepency. However the results of McInnes, Butcher and Clark show that there is a range of density where the quantitive error is quite small.

Testing the relationship of the conductivity exponent to the associated percolation problem yields an interesting result. We follow section 3.4.4 and put

$$R_{mn} = R_0\theta(2\alpha r_{mn} - s_0) \tag{4.2.15}$$

and seek the value of s_0 such that D(0) just vanishes, i.e. s_p. With

$$h(\omega, r_{mn}) = \frac{R_0\theta(2\alpha r_{mn} - s_0)\, n_s \exp(-\frac{4}{3}\pi n_s r_{mn}^3)}{R_0\theta(2\alpha r_{mn} - s_0) - i\omega} \tag{4.2.16}$$

$$\hat{h}_0 = \frac{R_0[1 - \exp(-\frac{4}{3}\pi n_s s_0'^3)]}{R_0 - i\omega} \tag{4.2.17}$$

is obtained, where $s_0' = s_0/2\alpha$, and using eqn.(4.2.7) we find

$$\gamma(\omega) = \frac{1}{i\omega}\left[\frac{i\omega - R_0\exp(-\frac{4}{3}\pi n_s s_0'^3)}{R_0 - i\omega}\right] \tag{4.2.18}$$

which yields in the limit $\omega \to 0$, $\gamma \to \infty$, i.e $D(0) \to 0$ for finite s_0 and $\gamma \to 1/R_0$ for $s_0' = \infty$. Therefore $s_p = \infty$.

It is not difficult to understand this result when we consider the physical nature of the approximation. Butcher (1974) relates it to a picture of hopping with site rerandomisation. Upon the arrival of the particle at a site, all the other sites in the system are redistributed at random. The co-ordinates governing the motion of the particle following its arrival at a site are statistically independent of those governing its previous motion. Recall

that in chapter 3 we related the process of current limiting, essential for the application of percolation theory, to the existence of correlated back-hopping. This process is obviously not included in the present approximation. It is thus no surpise that the value of s_p differs from the conductivity exponent.

4.3 Self- Consistent Theory

It is clear from the analysis of the preceeding section that the essential physics of the random walk model in the d.c. limit can only be described when correlated back- hopping is allowed for. The complexity involved in direct summation of an extended class of terms in the Green's matrix expansion is prohibitive. One is therefore led to a renormalised theory with correlated back-hopping represented by an average "self-energy", determined self-consistently. This is the approach taken by Movaghar and co-workers which is developed in a lengthy series of papers (Movaghar et. al. 1980 a,b,c; 1981). The method is based on the generalisation of the exact solution for a class of Cayley Tree (Bethe Lattice) models. The result of their theory and the essential nature of the approximations invoked therein can be economically obtained from the formulation of a simple self- consistent theory and its subsequent extension by the use of the effective medium technique to be described in the next chapter.

The decoupling scheme in the last section led to the identification of a self- avoiding walk. The resulting expansion of the average Green's function then had a simple convolution structure and the series for $\hat{G}_{\underline{k}}$ was a

straightforwad geometric progression. In this context the renormalised perturbation expansion (RPE) of Anderson (1958) is an invaluable mathematical tool. The exact Dyson expansion of G_{mn} is reduced to a self- avoiding walk expansion by renormalising the "vertices", i.e. the (G^{o}_{mm}). The new vertices then represent the probability of not only waiting at site m without hopping but also correlated returns to that site via closed paths that contain it. This is formally accomplished by the introduction of a set of self- energies into the denominators of the (G^{o}_{mm}). The RPE for G_{mn} is

$$G_{mn} = G_{mm}\delta_{mn} + G_{mm}R_{mn}G^{(m)}_{nn} + \sum_{p\neq m,n} G_{mm}R_{mp}G^{(m)}_{pp}R_{pn}G^{(m,p)}_{nn} + \sum_{r\neq p,m,n} \cdots\cdots\cdots \qquad (4.3.1)$$

where

$$G^{(i,j,k\ldots)}_{mm} = \frac{1}{\sum_{n} R_{mn} - i\omega - \Delta^{(i,j,k\ldots)}_{m}} \qquad (4.3.2)$$

and the self energies $(\Delta^{(i,j,k\ldots)}_{m})$ each have a renormalised series expansion:

$$\Delta^{(i,j,k\ldots)}_{m} = \sum_{n\neq m,i,j,k\ldots} R_{mn}G^{(m,i,j,k\ldots)}_{nn}R_{nm} + \sum_{\substack{n\neq m,i,j,k\ldots \\ p\neq n,m\ i,j,k\ldots}} R_{mn}G^{(m,i,j,k\ldots)}_{nn}R_{np}G^{(n,m,i,j,k\ldots)}_{pp}R_{pm} + \Sigma \text{ etc.} \qquad (4.3.3)$$

Some explanation of the notation is probably neccessary.

G_{mm} is the full diagonal Green's matrix element; it is the causal Fourier transform of the probability of finding the particle at site m at time t which was created there at time zero. It includes all processes whereby the particle can hop away from and subsequently return to site m. $G_{nn}^{(m)}$ is the analogous quantity for site n except that site m is excluded as an intermediate site in these processes. $G_{mm}^{(m,p\ldots)}$ and $\Delta_m^{(i,j\ldots)}$ are similarly defined. Let us perform the partial average on eqn. (4.3.1), neglecting the correlation between G_{mm} and the other other quantities that appear. Then, given the functions

$$\gamma^R(\omega) = \langle G_{mm} \rangle \tag{4.3.4}$$

and

$$h^R_{(i)}(r_{mn},\omega) = n_s \langle R_{mn} G_{nn}^{(i)} \rangle, \tag{4.3.5}$$

and assuming that the restrictions on the indices in the summations in eqn. (4.3.1) have little effect when N is large, we see immediately that $\langle G_{mn} \rangle$ has the same convolution structure as in section 4.2, except the $\{h^R_{(i)}\}$ are all different. In order to make further progress we approximate the average of h by averaging the denominator of the $G_{nn}^{(i)}$; eqns. (4.3.4) and (4.3.5) become

$$\gamma^R(\omega) = \frac{1}{\langle \sum_n R_{mn} - \Delta_m \rangle - i\omega} \tag{4.3.6}$$

and

$$h^R_{(i)}(r_{mn},\omega) = \frac{n_s R_{mn}}{\langle \sum_{p\neq m} R_{np} - \Delta_n^{(i)} \rangle - R_{mn} - i\omega} \tag{4.3.7}$$

where we have neglected any dependence of Δ_n on r_{mn}. The

final approximation is to relace $\langle \Delta_m^{(i)} \rangle$ by $\langle \Delta_m \rangle$. The physical content in this is discussed below. Then, defining

$$S = \langle \sum_n R_{mn} - \Delta_m \rangle \tag{4.3.8}$$

and noting that N is large, we obtain the analogues of eqns. (4.2.3) and (4.2.4):

$$\hat{G}_{\underline{k}} = \frac{n_s^{-1}\delta^R}{1 - \hat{h}^R_{\underline{k}}} - n_s^{-1}\delta^R \tag{4.3.9}$$

where

$$\delta^R(\omega) = \frac{1}{S - i\omega} \tag{4.3.10}$$

and

$$h^R(r_{mn},\omega) = \frac{n_s R_{mn}}{S + R_{mn} - i\omega} \tag{4.3.11}$$

It remains now to determine S and this is straightforward. The function S appears in the diagonal and off-diagonal parts of G_{mn} and it must be chosen so that the sum rule eqn. (4.1.6) is satisfied. We then obtain

$$\hat{h}^R_{\underline{0}} = 1 + i\omega\delta^R(\omega) \tag{4.3.12}$$

which is the self-consistency equation for S:

$$S = n_s \int d\underline{r}_{mn} \frac{(S - i\omega)R_{mn}}{S + R_{mn} - i\omega} \tag{4.3.13}$$

The analogous result to eqn. (4.2.9) is

$$\langle D(\omega) \rangle = \frac{n_s}{2d} \int d\underline{r}_{mn} r_{mn}^2 \frac{(S - i\omega)R_{mn}}{S + R_{mn} - i\omega} \tag{4.3.14}$$

where

$$dr_{mn} = n(2r_{mn})^{d-1}$$

This theory will be improved before we attempt a comparison with computer simulation data; it is nevertheless of interest to effect a comparison with the asymptotic conductivity formulae.

Inspection of eqn. (4.3.14) in the limit $\omega \to \infty$ shows that it yields the exact formula. As $n_s \to \infty$, $S \to \infty$ and the exact result is also obtained. Substituting $R_{mn} = R_0 \exp(-2\alpha r_{mn})$ into the equation and using the approximation for small S given in Appendix A, appropriate to the low density limit, we readliy find that S, which is a factor in $\sigma(0)$ is approximately $\exp(-q)$ where

$$q = \left[\frac{6\alpha^3}{\pi n_s} \right]^{1/3} \qquad (4.3.15)$$

in three dimensions and

$$q = \left[\frac{4\alpha^2}{\pi n_s} \right]^{1/2} \qquad (4.3.16)$$

in two dimensions. These differ from the percolation exponents in the appearance of the factor unity in place of N_p. Substitution of $R_{mn} = R_0\theta(2\alpha r_{mn} - s_0)$ into eqn. (4.3.13) shows that S vanishes linearly when $s_0 = q$. Thus $q = s_p$ and the qualitative predictions of this theory are completely in accord with percolation theory. However its failure to reproduce the correct coefficients in the exponents implies a large quantitative discrepency at low densities. It is also important to note the dimensionality dependence which enters into the correct conductivity exponents via N_p and which is

missing in this theory. The physical content of the approximations made above are clear when we note that, within a mean- field approximation, it is exact for a system with the topology of an N- fold co-ordinated Cayley Tree when $N \to \infty$. On this lattice there are no closed loops, the only renormalising contributions to G_{mm} come from back and forth hopping along the branches of the tree. Consequently all terms on the right hand side of eqn (4.3.3) apart from the first, vanish identically. Furthermore $G_{nn}^{(m,i,j\ldots)} = G_{nn}^{(m)}$ since if transfer is excluded to site m, there is then no path to any sites beyond site m. Therefore there are only two self enegies Δ_m and $\Delta_n^{(m)}$. The former is given by

$$\Delta_m = \sum_n \frac{R_{mn}^2}{\sum_p R_{np} - \Delta_n^{(m)} - i\omega} \qquad (4.3.17)$$

and the latter by a similar equation with the site m excluded from the summation. We argue here that in the limit $N \to \infty$ this difference becomes negligible within the context of a configuration average. Furthermore, adding $\sum_n R_{mn}$ to both sides of eqn. (4.3.17) and applying the configuration average in the way described above, equation (4.3.13) is regained.

The associated percolation problem can be related to a bond- percolation problem on a Cayley Tree. By this we mean a network of bonds which are either present or absent with probabilities p and 1-p respectively. It is a d.c. hopping conductivity problem where the (R_{mn}) have the probability distribution

$$\rho(R_{mn}) = p\delta(R_0 - R_{mn}) + (1 - p)\delta(R_{mn}) \qquad (4.3.18)$$

a bonding probability p can be defined for the R- hopping percolation problem by noting that two sites are connected if they lie within a distance $s_0' = s_0/2\alpha$ apart. In three dimensions p is then given by the probability of finding a site in a sphere of radius s_0 constructed around an arbitrary site i.e.

$$p = \frac{4}{3} \pi s_0'^3 / \Omega \qquad (4.3.19)$$

The bond percolation problem on a Cayley Tree is well understood (Essam, Sondheimer and Place 1974, Stinchcombe 1973) and in particular it is known exactly that the critical value of p for the formation of an infinite connected cluster, p_c, is given by

$$p_c = \frac{1}{Z - 1} \qquad (4.3.20)$$

where Z is the co-ordination number. Putting $Z = N \to \infty$ we find that the critcal value of s_0 is precisely that given by q in eqn. (3.4.15).

We have demonstrated that the value of s_p predicted by a theory can be found by solving the bond-percolation problem for an associated lattice, if this can be identified. This has two applications. When $\sigma(0)$ is calculated explicitly, we can check whether the theory is consistent with percolation theory in the d.c. limit. When $\sigma(0)$ is not calculated explicitly but the theory can be presumed to be consistent with percolation theory then we have an alternative route for the calculation of the d.c. conductivity exponent. We shall make use of this again.

In the low density limit when ω is non- zero, $S \to 0$ and

$$\langle G_{mn} \rangle' = \frac{R_{mn}}{-\omega^2 + i\omega R_{mn}}$$

This differs by a factor of 2 in the second term in the denominator from the pair approximation result eqn. (4.2.12); the quantitative effect is discussed in chapter 6. The failure of the theory to exactly reproduce the pair approximation is related to the neglect of the correlation between G_{mm} and the other terms in eqn.(4.3.1).

Let us now conclude the discussion of section 4.1 on the effects of including various correlation types. Suppose we neglect correlations of the first type in this theory. We then replace the $\langle R_m \rangle$ by statistically independent values. In the light of what will follow now, we need not concern ourselves with models for their probability distribution. Within the averaging procedure we have adopted, the function $h^R(r_{mn},\omega)$ becomes $R_{mn}/(S - i\omega)$ and the S which satisfies the sum rule is equal to $\langle R_m \rangle$. Furthermore it immediately follows that $D(\omega)$ is independent of ω and given by $D(\infty)$. The result is of interest because the structure of the average Green's function's expansion is identical to that of the Matsubara Toyozawa (1961) theory of the tight binding problem in a random lattice. Their method involves an independent equation for the analogous quantity to S, derived from a diagrammatic method, but this approach is not available to us because the sum rule must be satisfied if the theory is to be physical. In any case the result is still $D(\infty)$ and the clear implication is that the diagrammatic methods of tight binding theory are not useful approaches for the hopping problem.

4.4 Discussion

We have developed systematic expansion, resummation and averaging techniques for the average Green's function the result has been a reasonably good desciption of the R- hopping model, but it is not correct in detail. A realistic picture of the d.c. limit resulted from the inclusion of a self- consistent element S in a two- site decoupling approximation. By virtue of the self- consistency of the theory, S reflects the level of correlation included in the decoupling; the two- site decoupling led naturally to the identification of a Cayley Tree as the implicit lattice assumption. This assumption was found to be responsible for the error in the d.c. conductivity exponents when compared with percolation theory.

A systematic extension of the theory would involve a more extensive level of correlation. A three site decoupling has been investigated (Gochanour et. al. 1979; Movaghar and Schirmacher 1981); the work of Movaghar and Schirmacher relatesit to the assumption of a branching triangular lattice. The increase in algebraic and statistical complexity is considerable and the numerical calculations of Gochanour et. al. imply that the quantitative improvement is very small. It therefore seems that in order to obtain the correct percolation exponents from a theory of this type, a very sophisticated approach is required. An aim of this thesis is to investigate the phenomenology of hopping conductivity; relatively simple conductivity formulae are desirable. In view of this we consider the extension of the formula obtained here by the effecive medium method, a less rigorous but more flexible approach.

An immense problem is immediately apparent if we attempt to generalise the methods of this chapter to the finite temperature, energy dependent case. The effective transition rates, eqn. (2.1.9), then depend on absolute as well as relative site co-ordinates. The convolution structure in the expansion of the average Green's function is not obtained and even the simplest decoupling approximation becomes beset with mathematical complexity. The only quantity discussed above that generalises easily is the self energy S, when calculated directly from the mean- field approximation to an assumed Cayley tree topology. This observation forms the basis of a full energy dependent theory within the effective medium approach; we discuss it in the next chapter.

CHAPTER 5 - UNIFIED THEORY BASED ON THE RANDOM WALK APPROACH 2: EFFECTIVE MEDIUM THEORY

5.1 Effective Medium Theory

In this chapter we describe the effective medium method. We use it in section 5.2 to extend the results of the previous chapter and, in section 5.3, to discuss a different class of random hopping systems. The fundamental postulate regarding its use in the former context is that the problem of hopping on a random lattice can map onto a problem of hopping on a Bravais lattice with some effective hopping rates. If these rates can be found the calculation of $D(\omega)$ is then entirely straightforward. We have found that there are two avenues of developement open to us.

The first approach is to notice that there are physical quantities associated with the effective medium. The effective rate R^{M}_{mn} is one such quantity; another is $G^{O(M)}_{mm}$, which is the Fourier transform of the probability that the particle waits at site m for time t without hopping away, and which, in the notation of chapter 4, we write as $\delta^{M}(\omega)$. The procedure adopted is to identify either of these quantities with appropriate averaged quantities in the random system. We call this "effective medium theory by association" and discuss it in section 5.2. Simple and economical derivations of the continous time random walk theory of Scher and Lax (1973) and the theory of Movaghar et. al. (ops. cit. chapter 4), which we hereafter refer to as the MRWA, are obtained.

The second approach requires that the Green's matrix for the random system be written in the form

$$G = G^M + G^M T G^M \qquad (5.1.1)$$

where G^M is the Green's matrix of the effective medium. Approximations to T can be found if G can be obtained by direct expansion about G^M. Since G^M is non-random, the application of the configuration average to eqn. (5.1.1) immediately reveals that $\langle G \rangle$ is identical to G^M if

$$\langle T \rangle = 0 \qquad (5.1.2)$$

which is an implicit equation for G^M. It is not immediately obvious what the form of the effective medium for a random lattice should be such that G is actually obtainable by direct expansion. Klafter and Silbey (1980) identify the random lattice as a finely spaced regular lattice with sites occupying lattice positions at random. They obtain a formal expression for an effective rate matrix which connects all lattice positions. The expression they obtain requires prior knowledge of G. Their work is useful in that it demonstrates the existence of the effective medium in this situation.

A class of model systems where an approximation to T for use in equation (5.1.2) may be easily obtained is provided by the problem of hopping on a spatially regular lattice with hop rates connecting nearest neighbours which are independently assigned random values. In section 5.3 we discuss these "random-bond lattice models". Kirkpatrick (1973) obtained an approximate solution of eqn. (5.1.2) in the d.c. limit; we extend his method to the general a.c. case.

A random-bond model can be related to the problem of hopping on a random lattice with a suitable choice of lattice constant and distribution of hop rates. We investigate the d.c conductivity exponents obtained when several different distributions are used and discuss the usefulness of the model in the context of the phenomenology of hopping conducivity.

5.2 Effecive Medium Theory by Association

5.2.1 R- Hopping Models

Let us establish some notation and derive $D(\omega)$ for the effective medium. G^M is defined by

$$(R^M - i\omega)G^M = 1 \tag{5.2.1}$$

where

$$R^M_{mn} = R^M_m \delta_{mn} - R^M_{mn} \tag{5.2.2}$$

with

$$R^M_m = \hat{R}^M_{\underline{0}} \tag{5.2.3}$$

and

$$\hat{R}^M_{\underline{k}} = \sum_n \exp(i\underline{k}.\underline{r}_{mn})\ R^M_{mn} \tag{5.2.4}$$

Furthermore if we define $\hat{G}^M_{\underline{k}}$ by

$$\hat{G}^M_{\underline{k}} = \sum_n \exp(i\underline{k}.\underline{r}_{mn})\ G^M_{mn} \tag{5.2.5}$$

it is immediately apparent that, by virtue of translation symmetry $\hat{R}^M_{\underline{k}}$ and $\hat{G}^M_{\underline{k}}$ are independent of m and

$$\hat{G}^M_{\underline{k}} = \frac{1}{\hat{R}^M_{\underline{0}} - \hat{R}^M_{\underline{k}} - i\omega} \tag{5.2.6}$$

Inversion symmetry demands that $\nabla_{\underline{k}}\ \hat{G}^M_{\underline{k}}\big|_{\underline{k}=\underline{0}}$ vanishes so that

applying eqn. (4.1.5) we obtain

$$D(\omega) = \frac{1}{2d} \sum_n r_{mn}^2 \, R_{mn}^M \tag{5.2.7}$$

Now

$$\delta^M(\omega) = \frac{1}{\hat{R}_{\underline{0}}^M - i\omega} \tag{5.2.8}$$

so that we may rewrite eqn. (5.2.7) as

$$D(\omega) = \frac{1}{2d} \langle r^2 \rangle \left(\frac{1}{\delta^M(\omega)} + i\omega \right) \tag{5.2.9}$$

where $\langle r^2 \rangle = (\hat{R}_{\underline{0}}^M)^{-1} \sum_n r_{mn}^2 R_{mn}^M$ is the mean square site separation in the disribution provided by R_{mn}^M.

Let us now adopt the idea, stated in the previous section, of the random system as a lattice with lattice constant a, whose positions are occupied at random. Let p be the occupation probability which is related to the site density by $p = n_s a^3$; the limit $a \to 0$ will be taken. Define a lattice position occupation indicator η_m which is unity if the lattice position m is occupied by a site and zero otherwise. With these definitions we can rewrite the unperturbed diagonal Green's matrix element in the random system as

$$G_{mm}^0 = \frac{1}{\sum_n \eta_n R_{mn} - i\omega} \tag{5.2.10}$$

Inspection of equations (4.3.2) and (4.3.3) reveals that the full, renormalised, diagonal matrix element can be written in the form

$$G_{mm} = \frac{1}{\sum_n \eta_n R_{mn}^R - i\omega} \tag{5.2.11}$$

For the sake of completeness let us also rewrite eqn. (5.2.8) as

$$\gamma^M = G^{0(M)}_{mm} = \frac{1}{\sum_n R^M_{mn} - i\omega} \qquad (5.2.12)$$

The method of association is to equate quantities in the effecive medium with average quantities in the random medium. The Scher and Lax theory models the random lattice by a regular lattice with a distibution of waiting times at each site given by the distribution of the (G^0_{mm}). When the final congfiguration average is performed the result is identical to that obtained from equating $G^{0(M)}_{mm}$ with $\langle G^0_{mm} \rangle$, i.e. putting $\gamma^M = \gamma$. By associating $\langle r^2 \rangle$ with the mean square nearest neighbour separation, R^M_{mn} itself need not be identified and this, as we observed in section 4.2, is the approximation made by Scher and Lax. It is interesting to note that ~~constructing~~ constructing an effective medium with a hop rate $(1/\gamma - i\omega)$ connecting nearest neighbours only and setting a equal to $\langle r^2 \rangle$, leads to exactly the same result.

Consider now methods for identifying R^M_{mn} . Firstly we compare eqn. (5.2.10) with eqn. (5.2.12) and put

$$R^M_{mn} = \langle \eta_n R_{mn} \rangle' = pR_{mn} \qquad (5.2.13)$$

where the prime indicates an average over all stochastic variables (including the occupancy of site n) except for r_{mn}. Substituting into eq. (5.2.7) and taking the limit $a \to 0$ in which

$$\sum_n \to \int \frac{dr_n}{a^3} \qquad (5.2.14)$$

yields the result $D(\omega) = D(\infty)$, i.e the "no correlation" result obtained in section 4.1.

The theory discussed in section 4.3 provides an approximation to R^R_{mn} in eqn. (5.2.11). From equation (4.3.2) we see that

$$\sum_n \eta_n R^R_{mn} = \sum_n \eta_n R_{mn} - \Delta_m \qquad (5.2.15)$$

The decoupling procedure that was adopted was consistent with equation (4.3.17) for Δ_m. The averaging procedure that was adopted leads to the replacement of the terms $\sum_{p\neq m} R_{np} - \Delta_n^{(m)}$ in the denominator of that equation by the average quantity S. We may therefore identify R^R_{mn} as

$$R^R_{mn} = \frac{R_{mn}(S - i\omega)}{R_{mn} + S - i\omega} \qquad (5.2.16)$$

where S is determined self-consistently by

$$S = \langle \sum_n \eta_n R^R_{mn} \rangle \qquad (5.2.17)$$

We can now perform an association by putting

$$R^M_{mn} = \langle \eta_n R^R_{mn} \rangle' = p R^R_{mn} \qquad (5.2.18)$$

and it is immediately apparent that the resulting effective medium approximation, in the limit $a \to 0$, is identical to the self-consistent theory obtained in section 4.3.

The MRWA consists of an approximation to R^R_{mn} for use in eqn. (5.2.18) which is subtly different from eqn. (5.2.16). Recall that equation (4.3.17) was obtained when we identified

yields the result $D(\omega) = D(\infty)$, i.e the "no correlation" result obtained in section 4.1.

The theory discussed in section 4.3 provides an approximation to R^R_{mn} in eqn. (5.2.11). From equation (4.3.2) we see that

$$\sum_n \eta_n R^R_{mn} = \sum_n \eta_n R_{mn} - \Delta_m \qquad (5.2.15)$$

The decoupling procedure that was adopted was consistent with equation (4.3.17) for Δ_m. The averaging procedure that was adopted leads to the replacement of the terms $\sum_{p\neq m} R_{np} - \Delta_n^{(m)}$ in the denominator of that equation by the average quantity S. We may therefore identify R^R_{mn} as

$$R^R_{mn} = \frac{R_{mn}(S - i\omega)}{R_{mn} + S - i\omega} \qquad (5.2.16)$$

where S is determined self-consistently by

$$S = \langle \sum_n \eta_n R^R_{mn} \rangle \qquad (5.2.17)$$

We can now perform an association by putting

$$R^M_{mn} = \langle \eta_n R^R_{mn} \rangle' = p R^R_{mn} \qquad (5.2.18)$$

and it is immediately apparent that the resulting effective medium approximation, in the limit $a \to 0$, is identical to the self-consistent theory obtained in section 4.3.

The MRWA consists of an approximation to R^R_{mn} for use in eqn. (5.2.18) which is subtly different from eqn. (5.2.16). Recall that equation (4.3.17) was obtained when we identified

the self-consistent approximation to S as a Cayley tree approximation; we considered the first term in the RPE for Δ_m, the self-energy at site m. Let us define a site dependent quantity S_m whose configuration average in the self-consistent approximation is S. By adding $\sum_n R_{mn}$ to both sides of equation (4.3.17) we obtain the following expression for S_m:

$$S_m = \sum_n \frac{R_{mn}(S_n^{(m)} - i\omega)}{R_{mn} + S_n^{(m)} - i\omega} \qquad (5.2.19a)$$

where for convenience of notation we now redefine the summation to be over the sites in the system rather than positions in the underlying lattice and where

$$S_n^{(m)} = \sum_{p \neq m} R_{np} - \Delta_n^{(m)} \qquad (5.2.19b)$$

and we recall that $\Delta_n^{(m)}$ is the self energy at site n with transfer excluded to site m. To regain the self-consistent theory we put $S_n^{(m)} = S_n = S$ and average both sides. The essence of the MRWA is that the difference betweem $S_n^{(m)}$ and S_n is not neglected. From eqn. (5.2.19) we can identify R_{mn}^{R} and make the association with the effective medium by putting

$$R_{mn}^{M} = p \frac{R_{mn}(S' - i\omega)}{R_{mn} + S' - i\omega} \qquad (5.2.20)$$

where $S' = \langle S_n^{(m)} \rangle$

Using eqn. (4.3.3) we find that $S_n^{(m)}$ is given by

$$S_n^{(m)} = \sum_{p \neq m} \frac{R_{np}(S_p^{(n)} - i\omega)}{R_{np} + S_p^{(n)} - i\omega} \qquad (5.2.21)$$

Neglecting the restiction on the indices in the summation,

an apparently innocuous approximation in the thermodynamic limit, again returns us to the Cayley tree approximation. But implicit in the definition of $S_p^{(n)}$ is a restriction on an additional site index, distinct from site m. Similarly $S_p^{(n)}$ is defined in terms of another such quantity, $S_q^{(p)}$ say, implicit in whose defintion there is a restriction on another distinct site index. In this way the approximation (5.2.19) to S_m is established as a self-avoiding walk expansion and there are N! such walks in the system. Associated with the Cayley tree approximation are N^N self-avoiding walks, Movaghar and Schirmacher (1981) notice this as a source of error and present a partial iteration scheme, designed to attempt the correct counting of the walks, and which we now describe.

Equation (5.2.21) is rewritten as

$$S_n^{(m)} = \sum_{p \neq m} \frac{R_{np}[1 - i\omega/S_p^{(n)}]\, S_p^{(n)}}{S_p^{(n)} + R_{np} - i\omega} \qquad (5.2.22)$$

The factor $S_p^{(n)}$ in the numerator is iterated upon N times to yield:

$$S_n^{(m)} = \sum_{m \neq p \neq q \neq \ldots} \cdots \sum \frac{R_{np}[1 - i\omega/S_p^{(n)}]\, R_{pq}[1 - i\omega/S_q^{(p)}] \ldots}{[S_p^{(n)} + R_{np} - i\omega][S_q^{(p)} + R_{pq} - i\omega] \ldots} \qquad (5.2.23)$$

The configuration average of this equation is taken; the quantities $(S_q^{(p)})$ are replaced by their averages, S'. Because the (R_{mn}) only depend on inter-site separations the average of the right hand side decouples into a product of N averages. Because of the restrictions on indices there

are N! terms so that

$$S' = \frac{N!}{\Omega^N} \left[\int dr_{-mn} \frac{R_{mn}[1 - i\omega/S']}{S' + R_{mn} - i\omega} \right]^N \qquad (5.2.24)$$

Taking the Nth root of this equation and using Stirling's approximation leads to the final result

$$S' = \frac{n_s}{e} \int dr_{-mn} \frac{R_{mn}(S' - i\omega)}{S' + R_{mn} - i\omega} \qquad (5.2.25)$$

Upon comparing this result with the self-consistent theory we see that the effect of the self-avoiding walk nature of the expansion of S_m is represented by a density reduction factor of e.

The consequences of eqn.(5.2.25) with regard to the d.c. conductivity are immediately apparent when we recall the analysis of section 4.3. In the low density limit we obtain conductivity exponents of the form predicted by percolation theory with $N_p^{(2)} = N_p^{(3)} = e$. Because $e \cong 2.7$ good agreement is expected in three dimensions; the graphical results presented in the next chapter comfirm this. However $N_p^{(2)} \cong 4.5$ so that progress has still to be made for agreement to be obtained in this case. It is ~~interesting~~ interesting to note that since $N_p^{(4)} \cong 2.1$, eqn. (5.2.25) does not become more accurate with increasing dimensionality as might be expected from the mean-field nature of the approximation. The lack of any dimensionality dependence in the value of N_p found in this theory implies an underlying topology of the branching network type. Let us seek to identify the lattice which has identical percolation properties to those predicted by eqn. (5.2.25). Identifying a bonding probability p in same way as in section 4.3 leads

to the prediction $Np_c = e$ for the critical percolation probability, p_c. In the light of the above discussion it would seem reasonable to postulate that the equivalent lattice is a diminishing Cayley tree. This is defined as follows.

Consider a Cayley tree in which the origin has potential bonds to N sites in the first coordination shell, each site in the first coordination shell has N - 1 potential bonds to sites in the second coordination shell, each site in the second coordination shell has N - 2 bonds to sites in the third coordination shell and so on. This defines the diminishing Cayley tree, it is finite and stops at the Nth coordination shell. We speak of "potential" bonds as we are concerned with the percolation problem that arises in the limit $N \to \infty$ when we say that each bond is present with probability p. Let us calculate the critical percolation probability p_c for this lattice.

We perform a calculation based on an extension of an argument given by Essam et. el. (1974). We write $Q_i(p)$ for the percolation probability of a sub-network emanating from the ith coordination shell i.e. $Q_i(p)$ is the probability that a continuous paths exists from some arbitrary site in the ith shell to the Nth shell. The probability that the sub-network is not connected is $1 - Q_i(p)$. If the initial bond in the sub-network is not connected (probability $1 - p$) then the sub-network is non-percolating with probability one; if it is connected then the sub-network is non-percolating only if all the sub-networks emanating from it are themselves non-percolating. Hence

$$1 - Q_i(p) = 1 - p + p(1 - Q_{i+1})^{z_{i+1}} \qquad (5.2.26)$$

where $z_i = N - i$ is the coordination number of the sites in the ith shell. When $i = N - 1$ we have $z_i = 1$ and $Q_{N-1} = p$. We may use this initial condition to iterate on eqn. (5.2.26) and calculate $Q_1(p)$. Then the probability that the origin is connected to the Nth shell is

$$P(p) = 1 - [1 - Q_1(p)]^N \qquad (5.2.27)$$

since there are N potential bonds emanating from the origin. We have calculated P(p) for N = 100, 1000 and 10,000; the results are plotted in figure 2. It is clear that as N becomes large P(p) is zero for $p < e/N$ and that when $p > e/N$ P(p) rises rapidly to values in the order of unity. We conclude that $Np_c = e$; our above postulate is therefore confirmed.

The above calculation was originally performed by Summerfield and Butcher (1981) who found $Np_c = 1.5$. However, Straley (1981) pointed out the possibility of an instability in the numerical procedure used in that calculation and suggested an improved technique that we have used to derive the values plotted in figure 2.

Moraal (1982) has shown that $Np_c \geq e$ is an exact inequality for the diminishing Cayley tree.

5.2.2 Energy Dependent Model

We now describe the derivation of the energy dependent MRWA within the effective medium formalism. It is convenient to define, purely as a notational device, an

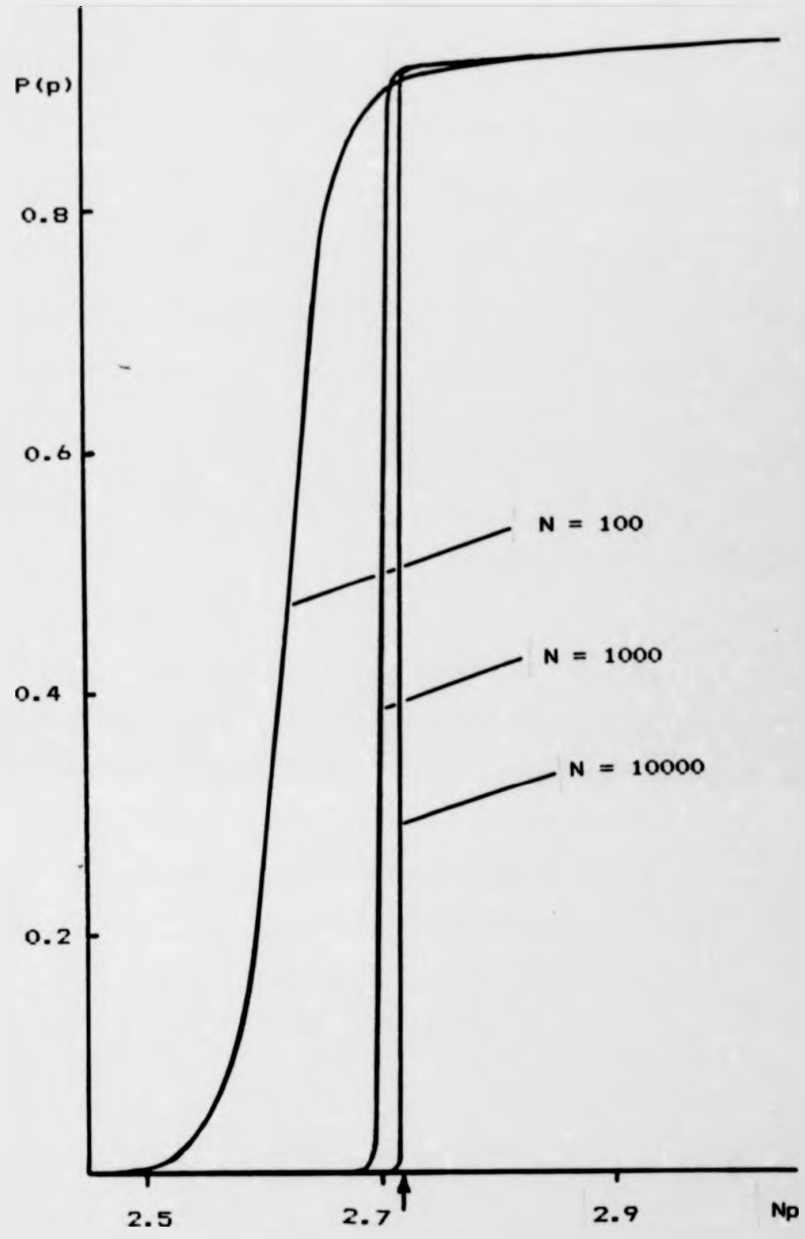


FIGURE 2

The percolation threshold of a diminishing Cayley tree. For various values of initial site coordination number N, the percolation probability P(p) is plotted against Np. The arrow marks the point where Np = e.

energy dependent diffusion coefficient $\bar{D}(\epsilon)$, defined such that

$$\langle D(\omega)\rangle = n_s^{-1} \int \rho(\epsilon)\bar{D}(\epsilon)d\epsilon \qquad (5.2.28)$$

In terms of this quantity $\langle\sigma(\omega)\rangle$, defined in section 2.2, is given by

$$\langle\sigma(\omega)\rangle = e^2\beta \int \rho(\epsilon)F(\epsilon)\bar{D}(\epsilon)d\epsilon \qquad (5.2.29)$$

where, we recall, $F_m = F(\epsilon_m)$ is the effective equilibrium occupation probability of the site m.

$\bar{D}(\epsilon)$ can be obtained from equation (5.2.7) with the identification of an appropriate energy dependent effective hop rate $R^M_{mn}(\epsilon)$.

In an energy dependent model we can calculate $S(\epsilon_m)$, which is S_m averaged over all variables except for the site energy ϵ_m, via the Cayley tree approximation to equation (5.2.19). We note that R_{mn} is now asymmetric and depends on r_{mn}, ϵ_m, and ϵ_n. The approximation yields

$$S_m = \sum_n \frac{R_{mn}(S_n - i\omega)}{R_{nm} + S_n - i\omega} \qquad (5.2.30)$$

It is useful to multiply by F_m, both sides of this equation and by F_n, the denominator and numerator on the right hand side. The symmetrical quantity Γ_{mn}, defined by equation (2.1.5), may then be used. Replacing S_n by its configuration average $S(\epsilon_n)$ and averaging both sides of eqn. (5.2.30) over all variables except for ϵ_m leads to the following integral equation for the quantity $F(\epsilon_m)S(\epsilon_m)$:

$$F(\epsilon_m)S(\epsilon_m) = \int \rho(\epsilon_n)d\epsilon_n \int d\underline{r}_{mn} \left[\frac{1}{\Gamma_{mn}} + \frac{1}{F(\epsilon_n)S(\epsilon_n) - i\omega F_n} \right]^{-1} \quad (5.2.31)$$

When the analogy between eqn. (5.2.31) and eqn. (5.2.17) is established, the identification of R^R_{mn} becomes straightforward. The association with the effective medium via eqn. (5.2.18) then yields

$$F(\epsilon_m)R^M_{mn}(\epsilon_m) = p \int \rho(\epsilon_n)d\epsilon_n \left[\frac{1}{\Gamma_{mn}} + \frac{1}{F(\epsilon_n)S(\epsilon_n) - i\omega F_n} \right]^{-1} \quad (5.2.32)$$

Substituting this result into eqn. (5.2.7) and using eqns. (5.2.28) and (5.2.29) we finally obtain

$$\sigma(\omega) = e^2\beta \int \rho(\epsilon_m)d\epsilon_m \int \rho(\epsilon_n)d\epsilon_n \int d\underline{r}_{mn} r^2_{mn} \ldots\ldots$$

$$\ldots\ldots \left[\frac{1}{\Gamma_{mn}} + \frac{1}{F(\epsilon_n)S(\epsilon_n) - i\omega F_n} \right]^{-1} \quad (5.2.33)$$

This is the final result of the MRWA except that the original authors include the density reduction e^{-1} in eqn. (5.2.31) by analogy with eqn. (5.2.25). In fact the derivation of eqn. (5.2.25) does not go through in the energy dependent case because the N averages over eqn. (5.2.23) do not decouple. Furthermore, as we show in chapter 6, although a scaling factor in an equation of this form is all that is needed for the d.c. conductivity to follow an exponential dependence of the type predicted by percolation theory, this factor is not e^{-1}.

In considering the asymptotic limits discussed in chapter 3, it is apparent that the MRWA is exact in the

high density and high frequency limits. However, in the low density limit at non-zero frequencies, where the pair approximation is the exact result, the MRWA can be obtained in the notation of section 3.2 by neglecting the last term in Z_p, as defined by eqn. (3.2.7), and so shows some error.

Thus, in surveying the random walk approach to a unified theory we have identified the MRWA as the most successful theory to date. However its success in the d.c. limit is restricted to the special case of R- hopping in three dimensions. Furthermore, it fails to correctly reproduce the pair approximation when the site density approaches zero at a finite frequency. The correction of these defects would surely require a fairly sophisticated extension of the methods presented in this and the previous chapter. Rather than pursue this line we divert our attention to the equivalent circuit approach in order to see whether it can yield a successful theory which is at the same time uncomplicated. In the next chapter we present our investigations into this approach and formulate such a theory.

The final topic to be considered in our discussion of the random walk approach, the random-bond lattice model, is an aside to the main theme of this thesis, the development of a unified theory that allows the evaluation of the rate equation approach to transport in real systems. Nevertheless it is a theoretical model with considerable intrinsic interest which can relate, in a limited context, to the actual random system that we are interested in.

5.3 Random-bond Lattice Models

In this section we apply the direct effective medium technique, described in section 5.1, namely the identification of the T-matrix, to calculate the a.c. and d.c. hopping conductivity of a system where the sites are located on a regular Bravais lattice but the intersite hop rate, which is restricted to connecting nearest neighbours only, is a random variable. The method (Summerfield 1981) is a generalization to the treatment of the d.c. conductivity for such a system by Kirkpatrick (1973).

For the system under consideration, the diffusion coefficient eqn. (5.2.7) becomes

$$D(\omega) = \frac{1}{2d} Z a^2 \bar{R}^M \qquad (5.3.1)$$

where $\bar{R}^M$ is the value of the constant rate coupling nearest neighbours.

Let R be the matrix of randomly distributed nearest-neighbour hop rates and put

$$R = R^M - R^1 \qquad (5.3.2)$$

where R^M is the matrix defined in eqn. (5.2.1) By standard manipulations (Elliot, Krumhansl and Leath 1974) the T-matrix, defined in eqn. (5.1.1), can be written as

$$T = R^1(1 - G^M R^1) \qquad (5.3.3)$$

We now seek an approximate solution to the equation (5.1.2) i.e. $\langle T \rangle = 0$. Adopting a bra-and-ket notation, where $|m\rangle$ represents the site m, R and R^M become

$$R = \sum_{mn}\sum |m\rangle(\delta_{mn} \sum_p R_{mp} - R_{mn})\langle n| \qquad (5.3.4)$$

$$R^M = \sum\sum_{mn} |m\rangle \bar{R}^M (Z\delta_{mn} - \Delta_{mn}) \langle n| \qquad (5.3.5)$$

where Δ_{mn} is defined to be unity if m and n are nearest neighbours and zero otherwise. R_{mn} has an independently distributed random value $\bar{R}$ when m and n are nearest neighbours and is defined to vanish otherwise. The perturbation R^1 may be written in the form

$$R^1 = \sum V_{mn} \qquad (5.3.6)$$

where $V_{mn} = |i\rangle\Delta\langle i|$; $\Delta = (\bar{R}^M_{mn} - R_{mn})$ and $|i\rangle = |m\rangle - |n\rangle$. The summation extends over all possible pairs of sites. Following Kirkpatrick we approximate T by the T-matrix obtained when just one rate is perturbed, t_{mn}, defined by

$$t_{mn} = V_{mn}(1 - G^M V_{mn})^{-1} \qquad (5.3.7)$$

and obtain

$$t_{mn} = \frac{|i\rangle\Delta\langle i|}{1 - \Delta F_{mn}} \qquad (5.3.8)$$

where

$$F_{mn} = \langle i|G^M|i\rangle = 2(G^M_{mm} - G^M_{mn}) \qquad (5.3.9)$$

where we have used the symmetry of the effective medium which, furthermore, upon taking the $\langle m|\ |m\rangle$ matrix element, of $G^M(R^M - i\omega) = 1$, leads to

$$F_{mn} = \frac{2(1 + i\omega G^M_{mm})}{Z\bar{R}^M} \qquad (5.3.10)$$

If the rates are distributed with probability distribution

$\rho(\bar{R})$ then, upon substitution of eqn. (5.3.10) into equation (5.3.8) and setting $\langle t \rangle = 0$, the following equation for $\bar{R}^M$ is obtained

$$\int \rho(\bar{R})d\bar{R} \frac{\bar{R}^M - \bar{R}}{(Z/2 - 1)\bar{R}^M + \bar{R} - i\omega(\bar{R}^M - \bar{R})G_{mm}} = 0 \quad (5.3.11)$$

which we shall refer to as simply the EMA.

Because V_{mn} in eqn. (5.3.7) satisfies eqn. (5.3.6) the method is of the homomorphic cluster type (Yonezawa and Odagaki 1978) and will thus yield a G^M with the correct analytic properties (Odagaki and Yonezawa 1978).

The EMA has been obtained independently by Bryksin (1980) and Odagaki and Lax (1981). The latter authors investigate the predictions for bond-percolation models and in particular find good agreement with their exact solution in one dimension. Both authors use the model for R- hopping systems by identifying a with the mean nearest neighbour separation and $\rho(R)$ with some distribution of hop rates in the random site system. Let us examine the consequences of this type of approach for the low density d.c. conductivity exponent. If we assume that the approximation supports the basic assertion of percolation theory (section 3.3.1), and this will be seen to be true, s_p can be found via the procedure that we established in section 4.3 i.e. relating the R-percolation problem to a bond-percolation problem.

For the bond percolation problem the prediction of the EMA is (Kirkpatrick 1973) $p_c = 2/Z$.

Put

$$\bar{R} = R_0 \exp(-2\alpha r) \quad (5.3.12)$$

and

$$\rho(\bar{R})d\bar{R} = n(r)dr \quad (5.3.13)$$

In considering the associated percolation problem and in particular the replacement $\bar{R} = R_0\theta(2\alpha r - s_0)$ we find that the related bond probability is

$$p = \int_0^{s_0/2\alpha} n(r)\, dr \qquad (5.3.14)$$

thus s_p is a solution of

$$p_c = \int_0^{s_p/2\alpha} n(r)\, dr \qquad (5.3.14)$$

We can now easily examine the effect of various forms of $n(r)$. Firstly we let $n(r)$ be the probability of finding any of N sites a distance r away from some reference site placed at the origin. Then $n(r) = d\lambda_d n_s r^{d-1}$ where $\lambda_2 = \pi$ and $\lambda_3 = 4\pi/3$ and it immediately follows that

$$s_p = \left[\frac{6p_c\alpha^3}{\pi n_s} \right]^{1/3} \qquad (5.3.16a)$$

in three dimensions and

$$s_p = \left[\frac{4p_c\alpha^2}{\pi n_s} \right]^{1/2} \qquad (5.3.16b)$$

in two dimensions. Comparison with the correct exponents reveals that N_p is replaced by p_c, which is less that unity and hence the source of a large error.

The next approximation is to divide up the solid angle around the reference site into Z quadrants and let $n(r)$ be the probability of finding a site a distance r away in any one particular quadrant. Thus we put $n(r) = d\lambda_d n_s r^{d-1}/Z$ and find that the ensuing approximation to N_p is $Zp_c = 2$. This

is a improvement over the previous result but is still incorrect and independent of dimensionality.

Finally we consider the form of n(r) that is used by Bryksin and Odagaki and Lax. It is the probability of finding the nearest neighbour to the reference site in any one quadrant a distance r away and given by

$$n(r) = [d\lambda_d n_s r^{d-1}/Z] \exp(-\lambda_d n_s r^d/Z) \qquad (5.3.17)$$

Substitution into eqn. (5.3.13) yields the same form for s_p with

$$N_p = Z\ln[1/(1-p_c)] \qquad (5.3.18)$$

$$= Z\ln[Z/(Z-2)] \qquad (5.3.19)$$

which is greater than unity and dependent on dimensionality in as much as Z varies among the types of Bravais lattice in two and three dimensions. The following results are found:

Two dimensions:

$N_p^{(2)} = 3.29$ hexagonal (Z = 3)

$= 2.77$ square (Z = 4)

$= 2.43$ triangular (Z = 6);

Three dimensions:

$N_p^{(3)} = 2.43$ simple cubic (Z = 6)

$= 2.30$ body centred cubic (Z = 8)

$= 2.18$ face centred cubic (Z = 12).

It is therefore not possible to find a lattice type that reproduces the correct values of $N_p^{(3)} \cong 2.7$ and $N_p^{(2)} \cong 4.5$.

Bryksin obtained the low density approximation to the solution of eqn. (5.3.11) and found an exponential of the form $\exp(-s_p)$ that our percolation analysis predicts.

It is of interest to note that exact values and numerical estimates are available for p_c in certain cases (the EMA is actually exact for a simple square lattice). The effect on N_p of using a better approximation than the EMA can therefore be predicted. The results are:

Two dimensions:

$N_p^{(2)} = 3.17$ hexagonal ($p_c = .653^{*}$)

$= 2.77$ square ($p_c = .500^{*}$)

$= 2.55$ triangular ($p_c = .347^{*}$)

Three dimensions:

$N_p^{(3)} = 1.73$ simple cubic ($p_c = .250^{**}$)

$= 1.56$ body centred cubic ($p_c = .178^{***}$)

$= 1.52$ face centred cubic ($p_c = .119^{***}$)

(*exact values, Sykes and Essam 1964; Kesten 1980; Wierman 1981)

(**Kirkpatrick 1979)

(***Shante and Kirkpatrick 1971)

These results show that the real situation in this model for R-hopping is in fact even worse than the EMA predicts.

In summary we note that the random bond lattice model, with the probability distributions used above, cannot accurately predict the d.c. conductivity exponents; more elaborate distributions could no doubt be postulated. Odagaki and Lax calculate the a.c. conductivity and show that it yields similar results to the Scher and Lax theory. It is not at all clear how the method can be realistically extended to deal with energy dependent systems. In chapter 7 we will show that a unified theory must be general enough to deal with them if real systems are to be considered. In the light of this it is not difficult to conclude that the

model is of limited applicability.

CHAPTER 6 - UNIFIED THEORY BASED ON THE EQUIVALENT CIRCUIT APPROACH

6.1 Introduction

Miller and Abraham's (1960) original formulation of the hopping conductivity problem was in terms of the equivalent circuit that we introduced in section 2.3. In the d.c. limit one is concerned with a random resistance network and this has been the motivation for much investigation into the properties of such networks (Kirkpatrick 1973; Stinchcombe 1973; Butcher 1975 etc.). In particular the application of percolation theory to these networks has been a most successful approach for hopping conductivity (ops. cit.). To date the possibility of using the equivalent circuit formulation for a unified theory has been neglected in favour of the random walk approach. This neglect is in fact unjustified, as we shall shortly demonstrate. The equivalent circuit formalism is a most useful approach and the method we shall employ readily yields a unified theory which represents a significant improvement over the results obtained from the random walk approach. We shall derive the extended pair approximation (Butcher and Summerfield 1981, Summerfield and Butcher 1982), hereafter referred to as the EPA. The theory is simple to develop and yields both analytic and numerical results, the asymptotic formulae discussed in chapter 3 are all regained in the appropriate limits and good agreement is obtained with the computer simulation data. The approximation method is distinct from those used in the last two chapters in that one is not concerned with the summation of a series nor with the identification of effective media. A simple and general conductivity formula follows immediately from a

straightforward mean-field approximation.

6.2 The Extended Pair Approximation

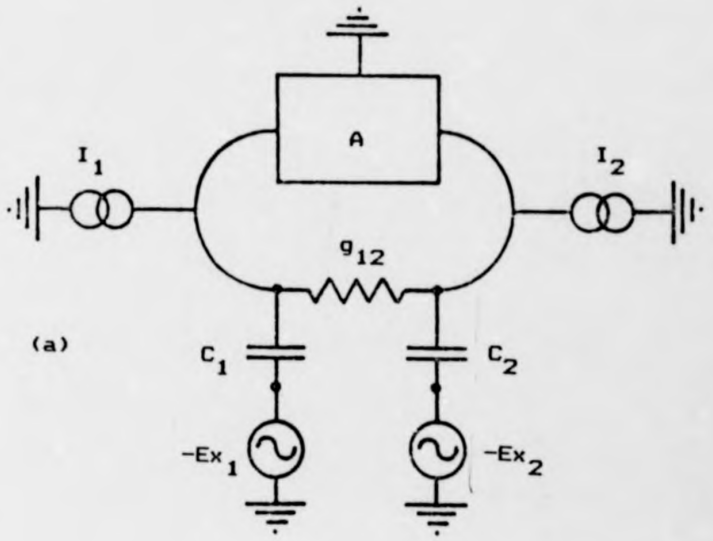
Recall that the linearised rate equations may be written in a form such that they are identical to Kirchoff's equations for an RC network (equations (2.3.1) and figure 1). Each site of the system corresponds to a node in the circuit and all nodes are mutually interconnected by the conductances $\{g_{mn}\}$, given by eqn. (2.3.2) and connected to earth by a series combination of a capacitor C_m ,eqn. (2.3.3) and a voltage generator $-Ex_m$. In section 2.3 we derived two conductivity formulae, eqn. (2.3.4) for the complex conductivity and eqn. (2.3.5) for its real part. In principle both are of equal use since the Kramers-Kronig relations can be used to find the imaginary part of $\sigma(\omega)$ when equation (2.3.5) is used. We prefer the simpler approach of using eqn. (2.3.4) which furthermore, as we show in section 6.4, leads to smaller errors in the approximation scheme that we employ. When we use equation (2.3.5) we find that $\langle\sigma(\omega)\rangle$ is obtained from knowledge of the voltage difference between an arbitrary pair of nodes, averaged over all system coordinates except for those pertaining to that pair.

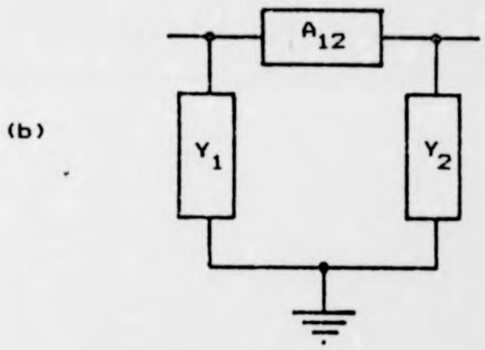
Consider a pair of nodes, which we label as 1 and 2. In section 3.3 we derived the pair approximation to the mean voltage difference $\langle V_{12}\rangle'$ by solving Kirchoff's equations when that pair is considered isolated. To go beyond the pair approximation, and in particular to obtain a finite d.c. conductivity, it is essential that the circuit external to the pair is taken into account. This we do by

replacing the external circuit by its average.

The effect of the external circuit on the pair 1 and 2 may be described by a two-port admittance matrix, A, and two current generators, I_1 and I_2, as shown in fig. 3a. The admittance matrix is symmetrical and may conveniently be given the π representation shown in fig. 3b. In principle we may determine the parameters of the external network (Y_1, Y_2, A_{12}, I_1, and I_2) by solving equations (2.3.1) for V_n with m and n taking all values except for 1 and 2, and substituting the results into equations (2.3.1) with m = 1 and 2. The parameters obtained in this way are functions of the positions and energies of all the sites. To develop a useful formalism we replace these fluctuating quantities by mean values depending only on ϵ_1 and ϵ_2. This is achieved, again in principle, by averaging over all other stochastic variables.

It is important to emphasise that we average the external network parameters over $\underline{r}_1$ and $\underline{r}_2$ because by doing so we achieve a tremendous simplification without much loss of accuracy. The simplification comes about because, in an infinite system, the mean values are dominated by contributions from configurations in which sites 1 and 2 are remote from each other and therefore decouple. Consider for example A_{12} which determines the current at site 1 produced by a voltage V_2 at site 2. We are concerned with an RC network at a non-zero frequency (ω = 0 may be approached as limiting case). Consequently, A_{12} falls to zero exponentially as $r_{12} \to \infty$ and its mean value is zero. The two sides of the π-network in fig. 3b are therefore decoupled by our averaging procedure and we arrive immediately at the simple network shown in fig. 3c. We have


A
I_1
I_2
g_{12}
(a)
C_1
C_2
$-Ex_1$
$-Ex_2$


A_{12}
(b)
Y_1
Y_2

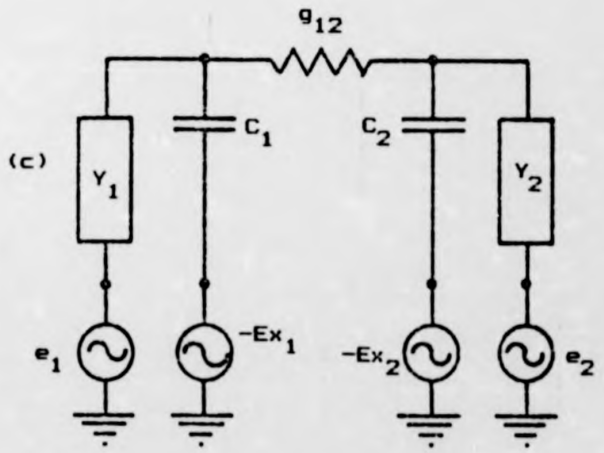

g_{12}
(c)
Y_1
C_1
C_2
Y_2
e_1
$-Ex_1$
$-Ex_2$
e_2

FIGURE 3 (preceeding leaf)

Reduction of the equivalent circuit to the extended pair approximation.

(a) General representation of the external circuit at an arbitrary pair of nodes.

(b) π representation of the two-port admittance matrix.

(c) Equivalent circuit for the extended pair approximation.

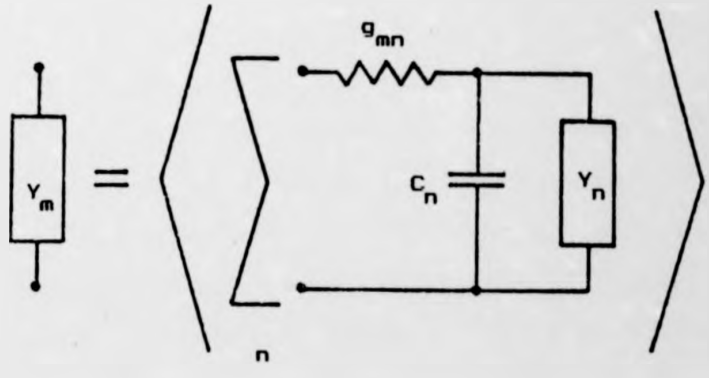


FIGURE 4

Schematic representation of the mean-field approximation to Y_m

replaced the current generators by equivalent voltage generators for convenience in the discussion to follow.

Kirchhoff's equations for the network shown in fig. 3c are

$$-i\omega C_1(V_1 + Ex_1) = -g_{12}V_{12} - Y_1[(V_1 + Ex_1) - (e_1 + Ex_1)] \tag{6.2.1a}$$

$$-i\omega C_2(V_2 + Ex_2) = g_{12}V_{12} - Y_2[(V_2 + Ex_2) - (e_2 + Ex_2)] \tag{6.2.1b}$$

where we have added and subtracted terms Ex_k on the right hand side. The terms in the round brackets are potential differences and thus independent of the origin of coordinates. It is not difficult to show that $Y_k(e_k + Ex_k)$ vanishes. We set k=1 to be definite and put the origin of coordinates at site 1. Then $x_1 = 0$ and we are concerned with Y_1e_1 which is the mean of the sum of the currents entering site 1 produced by the voltage generators $-Ex_n$ at all sites n except 1 and 2. We may extend the summation to include the currrent produced by the voltage generator at site 2 which is insignificant when 2 is remote from 1. Thus Y_1e_1 is the mean current entering site 1 due to the voltage generators at all site which are close enough to make a significant contribution. Let us examine the contributions to the mean from a particular configuration of sites and another configuration which is obtained from the first by reflecting all sites in the plane $x_1 = 0$. The two configurations have the same weight and the same intersite distances but the voltage generators $-Ex_n$ at each site (and their contributions to Y_1e_1) have opposite signs. Hence $Y_1e_1 = 0$ when $x_1 = 0$ and, since $Y_1(e_1 + Ex_1)$ is a potential difference, $Y_1(e_1 + Ex_1) = 0$ when $x_1 \neq 0$.

When we put $e_1 + Ex_1 = e_2 + Ex_2 = 0$ in eqn. (6.2.1) we find immediately that

$$V_{12} = \frac{-Ex_{12}}{Zg_{12}} \tag{6.2.2}$$

where

$$Z = \frac{1}{g_{12}} + \frac{1}{Y_1 - i\omega C_1} + \frac{1}{Y_2 - i\omega C_2} \tag{6.2.3}$$

Equation (6.2.2) differs from the pair approximation only in that Z replaces Z_p.

To complete the specification of the EPA we must calculate Y_1 and Y_2. Now Y_1, for example, is the external admittance seen from site 1 averaged over all stochastic variables except ϵ_1 and ϵ_2. It is in fact independent of ϵ_2 (and the presence or absence of site 2) because site 2 is usually remote from site 1. We may therefore write $Y_1 = Y(\epsilon_1)$ and, by the same argument, $Y_2 = Y(\epsilon_2)$. A suitable first approximation to $Y(\epsilon_1)$ is given by the mean field approach shown in fig. 4. The N - 1 conductances g_{mn} connecting site m to all other sites n and the associated capacitances C_n are taken into account exactly. The admittance of the rest of the network seen from site n is replaced by the mean value $Y(\epsilon_n)$. It is not difficult to see that writing down the algebraic equation that fig. 4 represents yields the same form as equation (5.2.30). We have already discussed that equation's prediction for the d.c. conductivity exponent. We now propose a simple approach to correct the deficiencies that we encountered previously. Replacing the admittance at site n on the right hand side of the equation in fig. 4 by its configuration average neglects the correlation between it and the

original admittance Y_m. Let us suppose that this can be allowed for by the introduction of a correction factor κ^{-1} on the right hand side of the mean field equation for $Y(\epsilon)$. We shall use the information that percolation theory provides to determine that factor. This is discussed in the next section, let us now simply write down our final result, the EPA equations. These are obtained by multiplying V_{12} by x_{12}, averaging over all possible orientations of the vector x_{12} and substituting into equation (2.3.6). When the system averages are written out explicitly, they are

$$\sigma(\omega) = \frac{1}{2d} \int d\epsilon_m \rho(\epsilon_m) \int d\epsilon_n \rho(\epsilon_n) \int dr_{mn}^2 \pi r_{mn} (2r_{mn}^{d-1}) \quad \ldots\ldots$$

$$\ldots\ldots \left[\frac{1}{g(\epsilon_m, \epsilon_n, r_{mn})} + \frac{1}{Y(\epsilon_m) - i\omega C(\epsilon_m)} + \frac{1}{Y(\epsilon_n) - i\omega C(\epsilon_n)} \right]^{-1} \tag{6.2.4}$$

where $Y(\epsilon)$ satisfies

$$Y(\epsilon_m) = \kappa^{-1} \int d\epsilon_n \rho(\epsilon_n) \int dr_{mn} \pi (2r_{mn})^{d-1} \ldots\ldots\ldots$$

$$\ldots\ldots \left[\frac{1}{g(\epsilon_m, \epsilon_m, r_{mn})} + \frac{1}{Y(\epsilon_n) - i\omega C(\epsilon_n)} \right]^{-1} \tag{6.2.5}$$

The site density n_s is the integral of the density of states $\rho(\epsilon)$. We see from equation (6.2.5) that $Y(\epsilon) \to \infty$ when $n_s \to \infty$. It follows from equation (6.2.4) that the correct asymptotic limit, as discussed in chapter 3, is obtained when either $n_s \to \infty$ or $\omega \to \infty$. Moreover, when $n_s \to 0$, $Y(\epsilon) \to 0$ and, upon comparing Z in equation (6.2.3) with Z_p in equation (3.2.7), we see that the pair approximation is regained.

6.3 Comparison with Percolation Theory

A detailed comparison of the EPA and the percolation theory approach to d.c. conductivity shows that, in all cases, the correction factor κ^{-1} introduced in section 6.2 must be constant and determines its value in an unambiguous way, independently of fitting any numerical conductivity data. This is accomplished by demanding that our approximate equations reproduce known percolation properties. To be explicit, we substitute equation (3.4.5), i.e. $g_{mn} = g_0\theta(s - s_0)$, into equation (6.2.5) and find the value of s_0 when Y just vanishes. By definition this is s_p and is a function of κ; we fix κ by requiring that this s_p be identical to that predicted by percolation theory. This procedure leads to accurate d.c. conductivity exponents because the factor $\exp(-s_p)$ is either explicitly contained in the solutions to the EPA equations or inferred from numerical studies. In section 3.4 we considered energy independent (R-hopping) and energy dependent models; here we determine κ for each case considered therein.

6.3.1 R- Hopping in d Dimensions

When we put $s = 2\alpha r$ and substitute $\omega = 0$ and $\rho(\epsilon) = n_s\delta(\epsilon)$ into equation (6.2.5) we immediately find that the EPA predicts

$$s_p = \left[\frac{6\kappa\alpha^3}{\pi n_s} \right]^{1/3} \qquad (6.3.1a)$$

in three dimensions and

$$s_p = \left[\frac{4\kappa\alpha^2}{\pi n_s} \right]^{1/2} \qquad (6.3.1b)$$

in two dimensions. These equations predict the known

percolation thresholds (3.4.4) if $\kappa = N_p$. We therefore set $\kappa = 2.7$ in three dimensions and $\kappa = 4.5$ in two dimensions. Moreover, considering now the d.c. R-hopping problem with the original exponential conductances $g_{mn} = g_0 \exp(-2\alpha r_{mn})$, the methods given in appendix A readily yield the result $Y = g_0 \exp(-s_p)$ when $n_s \to 0$. Since Y is a factor in $\sigma(0)$ we have complete agreement with the predictions of percolation theory.

6.3.2 Energy Dependent Model in Three Dimensions

We shall discuss the model defined in section 3.4.3 where, we recall

$$s = 2\alpha r_{mn} + (|\epsilon_m| + |\epsilon_n| + |\epsilon_m - \epsilon_n|)/2k_BT \qquad (6.3.2a)$$

$$\rho(\epsilon) = n_s/W \qquad |\epsilon| < W/2$$
$$= 0 \qquad \text{otherwise} \qquad (6.3.2b)$$

and where the approximation to s_p, obtained from a percolation theory approach, that leads to good agreement with computer simulation data, is given by

$$s_p = \left[\frac{40 N_p^{(4)} \alpha^3}{\pi \rho(\mu^*) k_B T} \right]^{1/4} \qquad (6.3.3)$$

Solution of the percolation problem by our equations is complicated by the fact that the admittance $Y(\epsilon)$ now has an energy dependence determined by a non-linear integral equation. However, we proceed by first reducing equation (6.2.5) to a non-dimensional form; we find, at low temperatures, that $Y(\epsilon) = g_0 y(x)$ where $x = \epsilon/k_BTs_0$ and $y(x)$ satisfies

$$y(x) = \xi \int_{-1}^{1} \frac{\theta[Q(x,x') - 1][1 - Q(x,x')]^3 y(x')}{1 + y(x')} dx' \qquad (6.3.4)$$

where

$$Q(x,x') = (|x| + |x'| + |x - x'|)/2 \qquad (6.3.5)$$

and

$$\xi = \frac{nk_B T \rho(\mu^*)}{6\kappa\alpha^3} s_0^4 \qquad (6.3.6)$$

with $\rho(\mu^*) = n_s/W$

We seek the critical value ξ_c of ξ for which the solution of the non-linear equation (6.3.4) approaches zero so that, from equation (6.2.4), $\sigma(0) = 0$. The corresponding value of s_p is the critical value of s_0 and is obtained by solving equation (6.3.6) with $\xi = \xi_c$. We find that

$$s_p = \left[\frac{6\kappa\xi_c\alpha^3}{n\rho(\mu^*)k_B T} \right]^{1/4} \qquad (6.3.7)$$

If κ is a dimensionless number then so too is ξ_c. therefore choosing κ as such is sufficient to reproduce the correct form of s_p. To determine ξ_c we neglect $y(x')$ in the denominator of the integrand in equation (6.3.4) since we are seeking a solution which vanishes as ξ approaches ξ_c. Then the equation becomes a linear eigenvalue problem which can be solved by standard methods.

We write equation (6.3.4) in the form

$$y(x) = \xi \int_{-1}^{1} K(x,x')y(x')dx' \qquad (6.3.8)$$

where

$$K(x,x') = \theta(Q - 1)(1 - Q)^3$$

It is clear that ξ_c is the minimum value of ξ for which there exists a non-trivial solution to equation (6.3.8). By inspection we see that $y(x)$ vanishes when $x = \pm 1$. Therefore we expand $y(x)$ in orthonormal functions with that property, specifically we put

$$y(x) = \sum_n a_n U_n(x) \tag{6.3.9}$$

and choose

$$U_n(x) = \cos[(2n-1)\pi x/2] \tag{6.3.10}$$

The quantities $\lambda = 1/\xi$ are the eigenvalues of the matrix K whose elements are given by

$$K_{mn} = \int_{-1}^{1} dx dx' \; U_m(x) K(x,x') U_n(x') \tag{6.3.11}$$

and we seek the maximum value of λ, λ_{max}. We have performed this calcuation numerically and found that taking the first 5 x 5 block of K is sufficient to give convergence in λ_{max} to three significant figures. We find $\lambda_{max} = 0.315$ and hence $\xi_c = 3.175$. Equation (6.3.7) therefore becomes identical to equation (6.3.3) if we choose $\kappa = 4.4$.

It is also ~~necessary~~ necessary to solve a non-linear integral equation to determine $Y(\epsilon)$ for energy dependent hopping with the original exponential conductances. At low temperatures we find that $g_0 \exp(-s_p)$, with s_p given above, is a good approximation to $Y(0)$. It follows from equation (6.2.4) that this factor also appears in $\sigma(0)$ as we confirm by the numerical results to be presented in section 6.5. Thus we again have complete agreement with the predictions of percolation theory but the energy dependence of $Y(\epsilon)$

prevents us from exhibiting this fact analytically.

6.4 Comparison with Random Walk Theory

When we compare the EPA equations to those of the MRWA it is remarkable that they are so similar because the techniques used in their derivations are quite different. In terms of the equivalent circuit $e^2\beta F_m G_{mn}$ is the voltage produced at site n when all the voltage generators are short-cicuited and a unit current is fed into site m. Hence the average admittance $Y(\epsilon)$ is related to the self energy $S(\epsilon)$ in the random walk approach by $Y(\epsilon) = e^2\beta F(\epsilon)S(\epsilon)$. The MRWA conductivity formula can be obtained from the EPA formula by neglecting the second term in equation (6.2.4). This difference does not have great quantitative effects, as we show in the next section, but it does imply, as we observed in chapter 5, that the MRWA does not reduce to the pair approximation at low site densities whereas the EPA reproduces it exactly. A more important difference, with regard to quantitative results, lies in the method of calculation of the self-energy (average admittance). Both theories start essentially from the mean- field approximation discussed in section 6.2 but Movaghar et. al. extend this treatment by the approximate iteration scheme we discused in section 5.2.2 and arrive at our equation (6.2.5) with κ replaced by e, independent of dimensionality and the form of s. We have already observed that this is only correct for R-hopping in three dimensions.

An important point to note is that in order to derive an extension of the random walk theory for R-hopping to the energy dependent case a generalisation which was essentially intuitive had to be made. In particular we refer to the

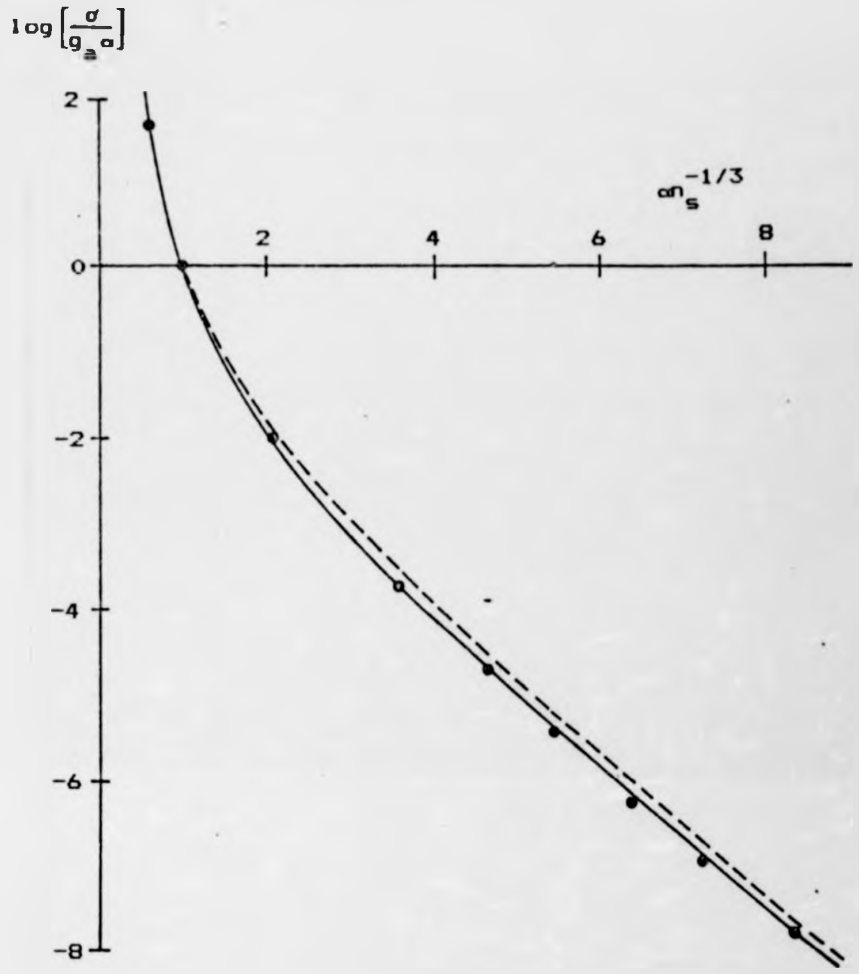


FIGURE 5

D.c. conductivity for the three dimensional R-hopping system with $\nu = 0$. The points are obtained from a full numerical solution of Kirchhoff's equations for 2500 sites (Butcher and McInnes 1978). The full curve is calculated numerically from the EPA equations and the dashed curve is the corresponding result calculated from the MRWA.

construction of the energy dependent effective medium in section 5.2.2. In contrast to this the EPA is completely general, the results for R-hopping are obtained as a special case.

It is interesting to observe that the site dependent quantity Y_m in the equivalent circuit analysis is exactly expressable in terms of another such quantity Y_n as can be seen from the construction that we used in figure 4 to derive the mean field approximation to its average. In fact Y_m and Y_n are related by an expression which is of the form of equation (5.2.30) for S_m. But the derivation of that equation required a selection of terms in the RPE for Δ_m. However, in the EPA approach the approximations that we make only relate to the method of calculating configuration averages. Because we are not concerned with perturbation expansions we do not meet the formal problem of convergence that is associated with them.

6.5 Results and Discussion

Using the values of κ obtained in section 6.3, we have solved equation (6.2.5) numerically for the special cases for which there exists computer simulation data on $\sigma(\omega)$.

We first consider the R-hopping model in d dimensions, defined by

$$\rho(\epsilon) = n_s \delta(\epsilon)$$

$$g_{mn} = g_a \exp(-2\alpha r_{mn} + \nu \ln \alpha r_{mn}) \qquad (6.5.1)$$

$$C_m = g_a / R_0$$

where R_0 is a chacteristic hopping frequency and $\nu = 0$ or $3/2$ in our numerical calculations. Y is independent of ϵ and equations (6.2.4) and (6.2.5) reduce to

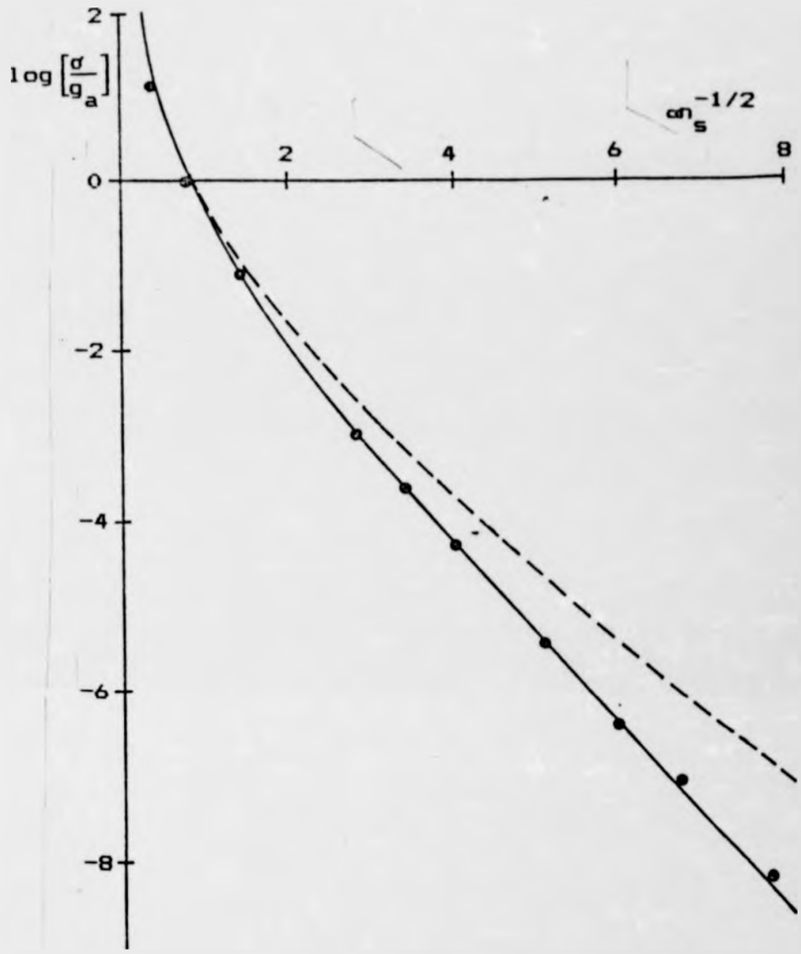


FIGURE 6

D.c. conductivity for the two dimensional R-hopping system with $v = 0$. The points are obtained from a full numerical solution of Kirchhoff's equations for 400 sites (Butcher, Hayden and McInnes 1977). The full curve is calculated numerically from the EPA equations and the dashed curve is the corresponding result calculated from the MRWA.

$$\sigma(\omega) = \frac{g_a m_s^2}{16 d \alpha^{d+2}} (\tilde{Y} - i\omega_1) \int_0^\infty dx\, x^4 \frac{\exp(-x + v\ln x/2)}{2\exp(-x + v\ln x/2) + \tilde{Y} - i\omega_1} \tag{6.5.2}$$

$$\tilde{Y} = \frac{m_s}{2\alpha^d} \kappa^{-1} (\tilde{Y} - i\omega_1) \int_0^\infty dx\, x^2 \frac{\exp(-x + v\ln x/2)}{\exp(-x + v\ln x/2) + \tilde{Y} - i\omega_1} \tag{6.5.3}$$

where $\tilde{Y} = Y/g_a$ and $\omega_1 = \omega/R_0$. The difference between these equations and those corresponding to the MRWA are the choice of κ in equation (6.5.3) and the factor 2 multiplying the exponential in the denominator in the integrand in equation (6.5.2). At high frequencies and densities both theories agree and are exact. For d.c. conductivity in three dimensions our results (calculated numerically with $v = 0$) are plotted in fig. 5 and compared with computer data and numerical solution of the MRWA result. Because the choice of κ is virtually the same in this case the results are very similar. The additional factor of 2 in equation (6.5.4) makes the EPA slightly smaller than the MRWA at low densitites, in better agreement with the data. In two dimensions (Figure 6) the EPA is a significant improvement over the MRWA because our choice of κ is correctly dependent on dimensionality.

Results for a.c. conductivity are presented in fig. 7 and 8. For the real part of $\sigma(\omega)$ the EPA is accurate in the d.c. limit but in the intermediate frequency range the curve is shifted slightly towards high frequencies because of the additional factor of 2 in equation (6.5.4) which effectively replaces ω in the MRWA by $\omega/2$. This discrepency becomes smaller as the site density is lowered because the EPA is tending towards the correct asymptotic limit. We expect that,

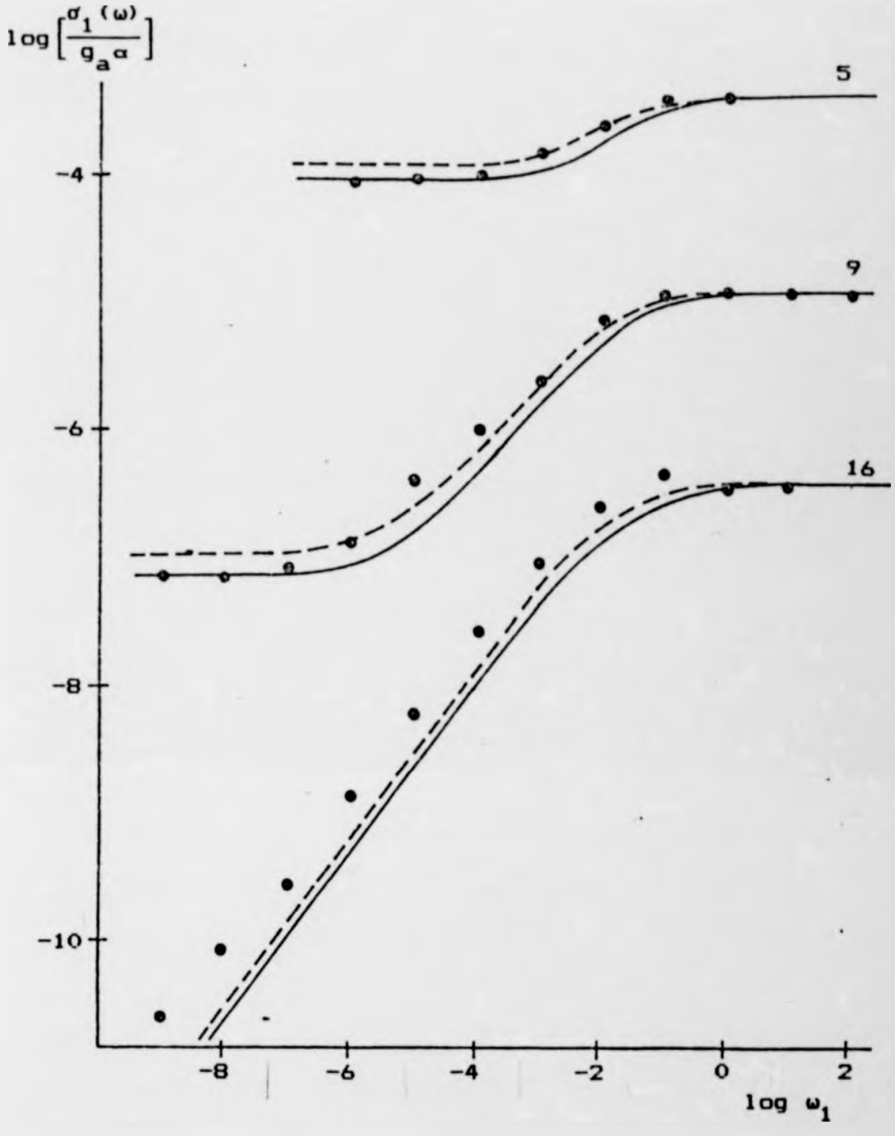


FIGURE 7

Real part $\sigma_1(\omega)$ of the a.c. conductivity for the three dimensional R-hopping system with $\nu = 3/2$ as a function of $\omega_1 = \omega/R_0$ for the values of $\alpha n_s^{-1/3}$ indicated. The points are obtained from a full numerical solution of Kirchhoff's equations for 1600 sites (McInnes, Butcher and Clark 1980). The full curves are calculated from the EPA equations and the dashed curves are the corresponding results calculated from the MRWA.

if data were available for extremely low densities, the EPA would be in good agreement at all frequencies.

The EPA is extremely accurate in the d.c. and high frequency limits. It is therefore of interest to examine the source of the error at intermediate frequencies. Two possibilities are: κ is determined in section 6.3 by considerations relating only to the d.c. conductivity and the effect of correlations in clusters of three or more conductances is neglected. The small error that could be due to the latter effect is illuminating in view of the considerable attention it has recieved in the literature (Boettger, Bryksin and Yashin 1979, Zvyagin 1980)

Let us turn out attention to the energy dependent system defined by equation (6.3.2). McInnes (1982) has recently performed a numerical study of the d.c. conductivity for this case with system parameters $\alpha n_s^{-1/3}$ = 3.4 and W = 10 meV. We have effected a numerical solution of equation (6.2.5) for the temperature and energy dependence of $Y(\epsilon)$. This is shown in fig. 9 and the corresponding values of $\sigma(0)$ are plotted in fig. 10 and compared with the computed conductivity. The agreement is good except in the high temperature range where the computed points are overestimates of the conductivity. This systematic error arises because the compuational procedure used by McInnes only takes into account the 12 largest conductances emanating from any particular site. The calculations of McInnes and Butcher (1978) indicate that increasing this number to 24 would decrease the discrepency apparent in fig. 10. This would, however, be at the expense of a considerable increase in computer time. In view of our inability to analytically exhibit the factor

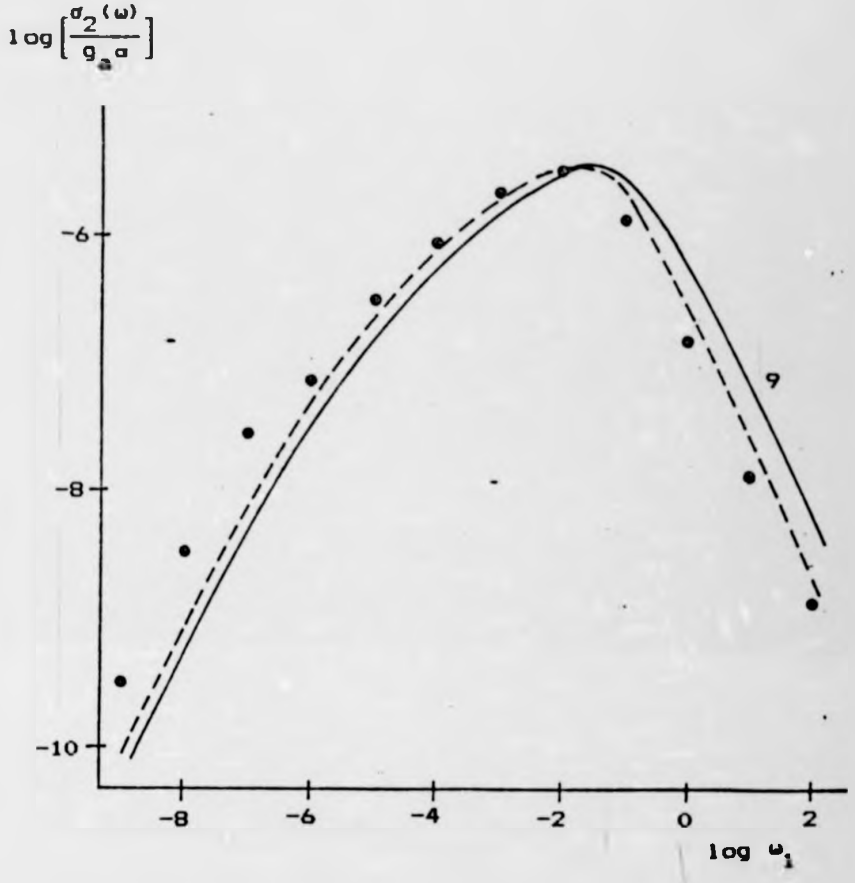


FIGURE 8

Imaginary part $\sigma_2(\omega)$ of the a.c. conductivity for the three dimensional R-hopping system with $\nu = 3/2$ as a function of $\omega_1 = \omega/R_0$ for the value of $\alpha n_s^{-1/3}$ indicated. The points are obtained from a full numerical solution of Kirchhoff's equations for 1600 sites (McInnes, Butcher and Clark 1980). The full curve is calculated from the EPA equations and the dashed curve is the corresponding result calculated from the MRWA.

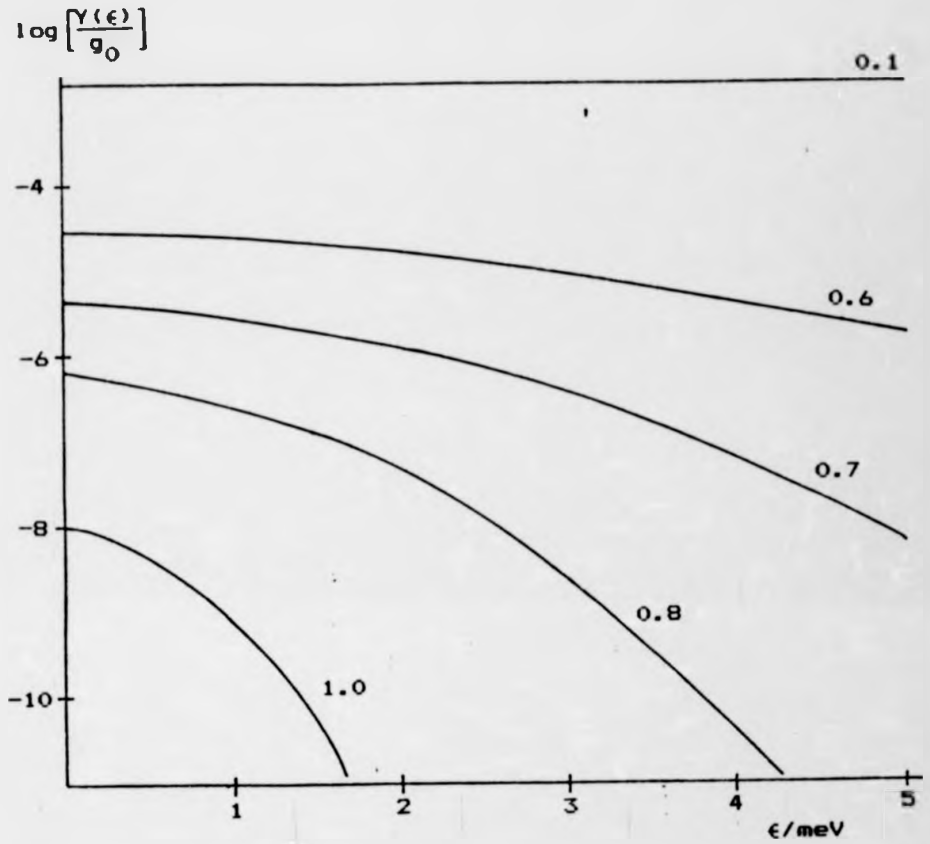


FIGURE 9

Y(ϵ) for the energy dependent model defined in the text plotted as a function of ϵ/meV for the values of $(T/K)^{-1/4}$ indicated when $\alpha n_s^{-1/3}$ and W = 10 meV.

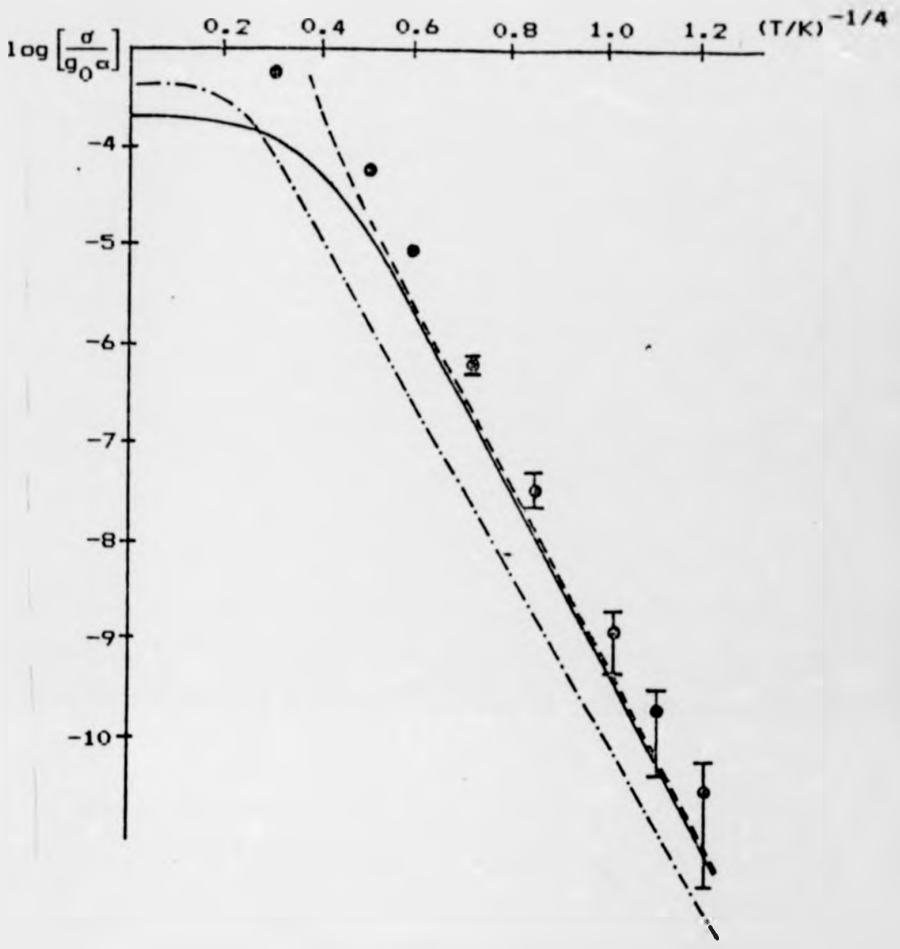


FIGURE 10

D.c. conductivity in three dimensions for the energy dependent model defined in the text and with the parameters of figure 9. The points are obtained from a full numerical solution of Kirchhoff's equations for 2197 sites (McInnes 1982). The full curve is calculated from the EPA equations. The dashed-dot curve is an interpolation between the low-temperature analytic approximation and the exact high temperature limit to the MRWA "barrier hopping" formula (Movaghar et. al. 1980c) and the dotted curve is calculated from the percolation formulae given by Butcher and Hayden (1977).

$\exp(-s_p)$ for the energy dependent case, we have also plotted the corresponding result from percolation theory (Butcher and Hayden 1978). The curves are remarkably close.

In examining the MRWA for this case it is useful to evaluate the accuracy of an approximation proposed by Movaghar et. al. (1980c) since they have used it in a comparison with experimental data. They reduce the problem to symmetrical "barrier-hopping", that is to say only energy differences appear in the conductances. A simplfication comes about because Y is then independent of energy. They claim that it is a valid approximation at low temperatures. We have calculated results from their conductivity formula for the system parameters under consideration and plotted them in fig. 10. There is a significant error which implies that the usefulness of the barrier hopping approximation is limited.

Penultimately, let us return to the discussion of the choice of conductivity formulae which we initiated in section 6.1. We have used the complex formula (2.3.4) and ignored the alternative formula (2.3.5) for the real part $\sigma_1(\omega)$ of $\sigma(\omega)$. In an exact treatment both formulae would yield the same value for $\sigma_1(\omega)$ but in the EPA they yield different results.

Using equation (6.2.2) for V_{mn} in equation (2.3.5) and setting $\omega = 0$ and $\nu = 0$ leads to, in three dimensions,

$$\sigma(0) = g_a \frac{\pi n_s^2}{48\alpha^5} \tilde{Y}^2 \int \frac{x^4 \exp(-x)dx}{[\tilde{Y} + 2\exp(-x)]^2} \qquad (6.5.4)$$

At low densities, when $\tilde{Y} \to 0$, the factor multiplying x^4 in the integrand in eqn. (6.5.4) is sharply peaked at $x = s_p$.

ln2 when $\tilde{Y} = \exp(-s_p)$. Hence we may take the slowly varying factor x^4 outside of the integral with its value at $x = s_p + \ln 2$ and the resulting integration is then trivial. We obtain

$$\sigma(0) = g_a \frac{\pi^2}{96a^5} [s_p + \ln 2]^4 \exp(-s_p) \qquad (6.5.5)$$

When $Y \to 0$ we have $s_p \to \infty$ and the ln2 term in the square brackets may be neglected. We now observe that this result is precisely one quarter of the value of $\sigma(0)$ found by Butcher, Hayden and McInnes (1977) in their percolation-theoretic approach. Their result was in good agreement with the computer simulation data and in fact our previous result is numerically very similar to it. Hence the error in using equation (2.3.5) is much greater than we have found above using equation (2.3.4). The reason is not hard to find. The EPA provides an approximation to the potential difference between an arbitrary pair of sites in which fluctuations due to variations in the external network have been removed, i.e. it yields an approximation to the mean potential difference which is what is required in equation (2.3.4). On the other hand, in equation (2.3.5) we require the mean of the squared magnitude of the potential difference, a quantitiy which is not calculated in the EPA. Replacing the mean square by the square of the mean would be expected to yield an under-estimate and that is precisely what we have found.

We have shown in this chapter that a systematic reduction of the general Miller-Abrahams equivalent circuit yields a simple extended pair approximation to $\sigma(\omega)$ which is in good agreement with asymptotic formulae and computer data. It is

at once surprising and gratifying that so simple a treatment should yield such good results. The analysis is open to improvement at some points but there is not much room for improvement in the quantitative predictions. The EPA formulae therefore provide a sound basis for an unambiguous analysis of experimental data in terms of the rate equation model. We take up this question in the next chapter.

CHATPER 7 - ANALYSIS OF EXPERIMENTAL DATA

7.1 Introduction

In this chapter we discuss the use of the Extended Pair Approximation in a comparison of the predictions of the Miller-~~Abrahams~~ Abrahams rate equation theory for a.c. and d.c. hopping conductivity with experiment (Summerfield and Butcher 1982). The accuracy of the EPA was established in chapter 6 by comparison with exact asymptotic conductivity formulae and computer simulation data; here we use it to analyse data on a range of physical systems in which hopping is presumed to be the dominant transport mechanism. We consider low temperature impurity conduction in n-type silicon (Pollak and Geballe 1961) in section 7.3 and in section 7.4 the similar effect in n-type gallium arsenide (Kahlert et. al. 1976 a,b) is discussed. Conduction in amorphous Germanium is considered in section 7.4.

7.2 Impurity Conduction and The R-Hopping Model

If the energy and temperature dependence of the individual conductances in the equivalent circuit can be subsumed into an overall scaling factor for $\sigma(\omega)$ and otherwise neglected, a great simplification results. This situation defines the R-hopping model and in chapter 6 we used it extensively in discussing the comparison of the EPA with computer simulation results. We recall that the conductances (2.3.2) are replaced by

$$g_{mn} = g_a(\alpha r_{mn})^s \exp(-2\alpha r_{mn}) \qquad (7.2.1)$$

and the capacitances (2.3.3) are given by

$$C_m = g_a/R_0 \qquad (7.2.2)$$

This would be the case, for example, in the limit $T \to \infty$ when g_a becomes $e^2\beta R_0 n(1 - n)$ where n is the electron density. The usual application of the R-hopping model to systems at finite T involves the inclusion of the activation factor $\exp(-\beta\epsilon_3)$ in g_a, we shall refer to this as the activated R-hopping model. There are conditions under which it is a good approximation and these relate exclusively to the d.c. conductivity. Shklovskii (1973) argues that for impurity conduction under conditions of weak compensation most of the donor states will be well away from acceptors and thus suffer a small spread in energy. He identifies the activation energy ϵ_3 as the energy required to remove a carrier (hole) from the vicinity of an acceptor. Having been thus freed, the carrier can then traverse the system via states which are approximately isoenergetic. To obtain this result from an analytic theory we must assume that $\rho(\epsilon)$ is sharply peaked at the unperturbed donor energy which we take to define the zero of energy. Then, in the EPA for example, at sufficiently high temperatures the factors other than $\rho(\epsilon)$ in the integrands in equations (6.2.4) and (6.2.5) will be relatively slowly varying and may be taken outside of the ϵ- integrals with their value at $\epsilon=0$. The result will be R-hopping with g_a containing the factor $\exp(-\beta\mu^*)$. The usual procedure at this point would be to identify μ^* with the experimental activation energy. However the electron density in an impurity band is fixed and given by $n = N_D - N_A$, where N_D is the donor density and N_A the acceptor density. We therefore have an equation for μ^*, namely:

$$\int \rho(\epsilon) f(\epsilon) d\epsilon = n \qquad (7.2.3)$$

where $f(\epsilon)$ is the electron eqilibrium occupation probability, equation (2.1.1). When $T \to \infty$ $f(\epsilon) \to n/N_D$ and hence

$$\mu^* \cong -k_B T \ln(N_D/n - 1) \qquad (7.2.4)$$

so that activation will only occur at sufficiently low temperatures such that μ^* does not behave in this way. It is clear then that in order for activated R-hopping to occur (and formulae of this type are successful e.g. Butcher, Hayden and McInnes 1977) the temperature scales governing the behaviour of μ^* and σ must be different. We cannot explicity define these scales but our numerical results in the next section support this inference. In another situation where activated R-hopping is a good approximation to $\sigma(0)$ these temperature scales can be defined.

Gel'mont et. al. (1975) and Hayden and Butcher (1978) study hopping in a rectangular band of finite width using percolation theory. They find that at high temperatures $\sigma(0)$ is activated and that in fact this behaviour persists until $T \sim W/k_B s_p^{\infty}$ where W is the bandwidth and s_p^{∞} is the conductivity exponent at $T = \infty$ which is ~10 for typical experimental systems. The solution of equation (7.2.3) is achieved in section 7.4 and we find that μ^* varies fairly slowly until $T \sim W/k_B$. Therefore in the temperature range $W/k_B \gtrsim T \gtrsim W/k_B s_p^{\infty}$ we would expect activated conductivity behaviour and this is confirmed by our numerical results in the section cited.

It is important to note that the considerations leading to the activated R-hopping ~~picture~~ picture relate only to the d.c. conductivity. This is confirmed experimentally by the

weaker dependences of a.c. conductivity that are usually observed. For the case of a peaked density of states it is neccessary to assume that the contribution to $\sigma(\omega)$ of the small number of states in the vicinity of μ^* is unimportant. Whilst this is true at $\omega = 0$ it is not true at high frequencies where such states make exponentially larger contributions than do those well away from μ^* (this can be easily seen by examining the form of the infinite frequency conductivity equation (3.2.3)). The physical understanding of this in the case of impurity conduction with low compensation is clear. For d.c. conductivity the carrier must be excited away from the acceptor in order to find paths through the whole system whereas a.c. loss can occur by carriers executing reciprocating motion in the vicinity of the acceptors. We therefore conclude that a unified theory of a.c. and d.c. conductivity can only in general describe real systems when formulated beyond the confines of the R-hopping framework. This is the approach we take in the rest of this chapter where we compare the predictions of the EPA with experimental data. In the next section we also compare with the prediction of a previous analysis based on an R-hopping model which we show to be inadequate.

7.3 Impurity Conduction in Doped n-Si with Low Compensation

We consider the extensive experimental results reported by Pollak and Geballe (1961) for their sample 13. The donor density $N_D = 2.7 \times 10^{17} cm^{-3}$, the compensation ratio is .003 and the experimentally observed activation energy of the d.c. conductivity is 6meV. Measurements were made over the

temperature range 1.7 to 20 K and the frequency range $0-10^5$ Hz. Previous attempts to analyse this data were on the basis of an R-hopping model Scher and Lax 1973, Odagaki and Lax 1981). However, its predictions are not entirely consistent with the data, as we now show.

Scher and Lax (1973, hereafter referred to as SL) have used their CTRW theory to interpret Pollak and Geballe's data. They employ the R-hopping approximation but in a different way to that descibed in the last section. The method of section 7.2 involved replacing $f(\epsilon)$ by $\exp(-\beta\epsilon_3)$, where ϵ_3 is the experimentally observed activation energy, and putting $\epsilon_1 = \epsilon_2$ in the ~~transiction~~ transition rates. Instead of this SL put $f(\epsilon) = N_A/N_D$ and remove the difficulty of energy disorder by averaging the energy difference in the rate. Specifically they approximate equation (1.1) by

$$R_{12} = R_0\beta(\epsilon_1 - \epsilon_2)\exp[-\beta(\epsilon_1 - \epsilon_2)](\alpha r_{12})^{\nu}\exp(-2\alpha r_{12}) \qquad (7.3.1)$$

where the appropriate value of ν for n-type silicon is 3/2. They replace $\epsilon_1 - \epsilon_2$ in eqn. (7.2.1) by an average energy separation, subsequently identified as ϵ_3. The idea that ϵ_3 is the energy separation between the Fermi level and the main peak of $\rho(\epsilon)$ is quite well established. In the light of this it is difficult to ~~conceive~~ conceive of ϵ_3 as simply an average energy separation calculated without regard to the Fermi level. Nonetheless, if the formalism is defined in this way it becomes identical to hopping in the $T \to \infty$ limit with rates of the form

$$R_{12} = R'_0\,(\alpha r_{12})^{3/2}\exp(-2\alpha r_{12}) \qquad (7.3.2)$$

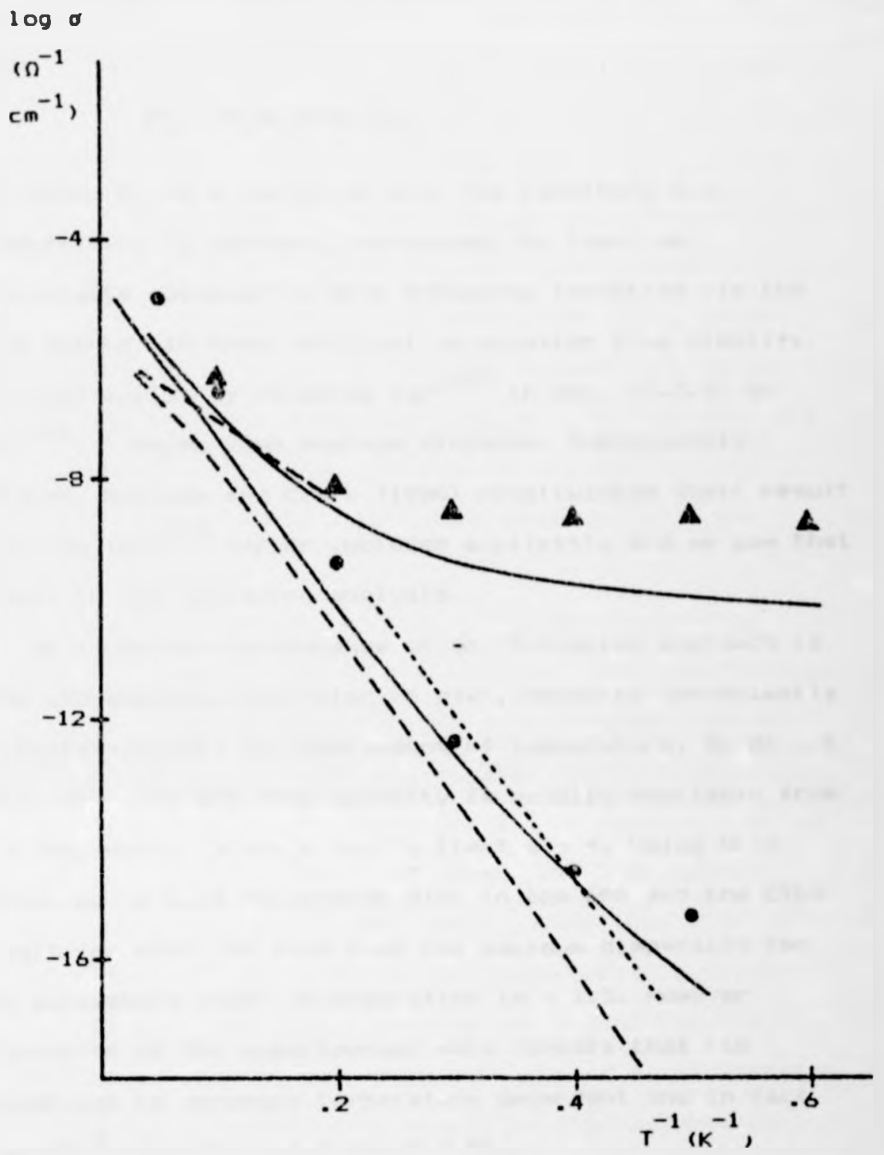


FIGURE 11

Comparison with impurity conduction in n-Si: Conductivity vs inverse temperature at two frequencies. The circles and triangles represent the experimental data at d.c. and 10^5Hz respectively (from Pollak and Geballe 1961). The lower and upper full curves are the results of the EPA at these frequencies. The lower and upper dashes curves are the corresponding results of the SL theory. The dotted curve is $\sigma(=)$.

with

$$R'_0 = R_0 \beta\epsilon_3 \exp(-\beta\epsilon_3)$$

and since R'_0 is a factor in $\sigma(0)$ the resulting d.c. conductivity is correctly activated. SL found an approximate solution to this R-hopping formalism via the CTRW method. In their original formulation they simplify the calculation by relacing $(\alpha r)^{3/2}$ in eqn. (7.3.2) by $(\alpha\bar{r})^{3/2}$, $\bar{r}$ being some average distance. Subsequently McInnes, Butcher and Clark (1980) recalculated their result with the $(\alpha r)^{3/2}$ factor included explicitly and we use that result in the following analysis.

An immediate consequence of any R-hopping approach is that the maximum dispersion in $\sigma(\omega)$, measured conveniently by $\log[\sigma(\infty)/\sigma(0)]$ is independent of temperature. SL do not calculate $\sigma(\infty)$ but this quantity is readily available from the EPA, which is exact in the limit $\omega \to \infty$. Using SL's formalism we have calculated $\sigma(\infty)$ in the EPA and the CTRW result for $\sigma(0)$. We find that the maximum dispersion for the parameters under consideration is ~ 1.3. However inspection of the experimental data reveals that its dispersion is strongly temperature dependent and in fact $\log[\sigma(10^5 Hz)/\sigma(0)] > 1.3$ for $T < 5K$.

In figs. 11 and 12 we plot the SL results as dashed lines together with the results of a calculation based on the EPA, details of which are given below. The steepest descent method used in the evaluation of an integral in the SL theory breaks down for $\omega/R'_0 \gtrsim 0.1$ and this point marks the termination of the dashed a.c. conductivity curves towards the right hand side of the figures. The theory works quite well for a combination of high temperatures and

low frequencies; in their original analysis SL selected data with T > 3.5 K. It is worthwhile pointing out that the R-hopping formalism used yields $\sigma(\infty)$ when $\omega/R'_0 \gtrsim 1$. Thus it predicts an activated, frequency independent conductivity in a regime in which the data is only weakly dependent on temperature and has a power law dependence on ω. These discrepencies are illustrated by the dotted $\sigma(\infty)$ curves in fig. 11 and 12 which start when $\omega/R'_0 = 1$. We see that the SL curves rise above $\sigma(\infty)$. This is an artifact of the steepest descent method used in the evaluation of the relevent integrals.

Odagaki and Lax used the effective medium method, described in section 5.3 to evaluate $\sigma(\omega)$ and undertook an analysis of data considered here. They obtained results which represent a definite improvement over the CTRW. However they used the SL formalism and consequently do not correct the deficiencies cited above. The alternative formalism of section 7.2 represents another way of using the CTRW approximation. Since the compensation is weak and k_BT is usually less than 1 meV the conditions for its applicability appear to prevail. The spreading of energies away from the isolated donor energy is attributable to compensation and thus expected to be small. However this approach would predict activated conductivity at all frequencies and this is simply not observed. Furthermore, we have examined this approach and find that, although the d.c. conductivity obtained is in fair agreement with the data, the a.c. conductivity does not rise above $\sigma(0)$ until about 10^5Hz.

Our conclusion concerning the R-hopping approximation is that it cannot be useful over the full temperature and

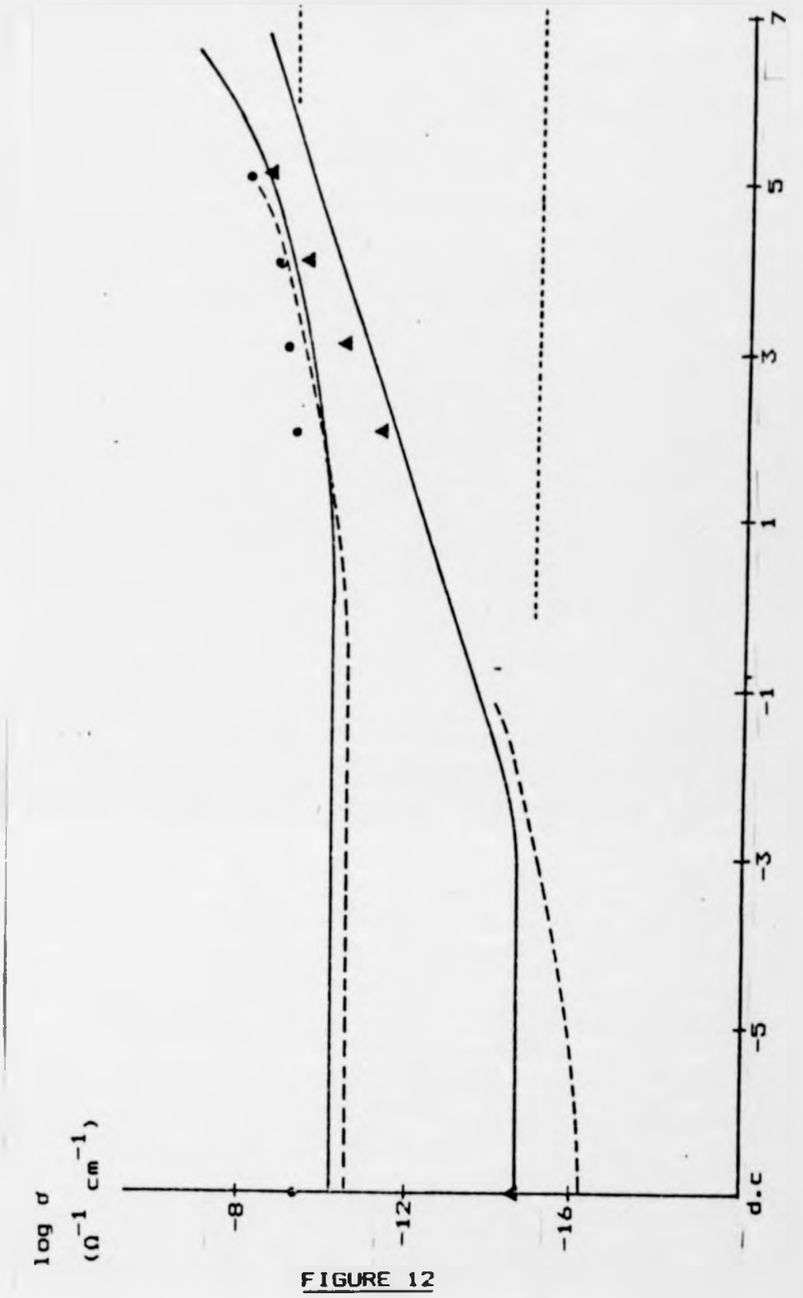


FIGURE 12

Comparison with impurity conduction in n-Si: conductivity vs frequency f at two temperatures. The circles and triangles represent the experimental data at 5 k and 2.5 K respectively. The upper and lower full curves are the results of the EPA at these temperatures. The upper and lower dashes curves are the corresponding results of the SL theory. The upper and lower dotted curves are $\sigma(\omega)$ for the two temperatures.

frequency range of Pollak and Geballe's data. We therefore approach the analysis of this data via the full EPA equations (6.2.4) and (6.2.5) with $g(\epsilon_m,\epsilon_n,r_{mn})$ given by equations (2.3.2) with (2.1.6), (2.1.1) and (1.2).
The input parameter in the EPA is now the energy dependence of the density of states function. Although the calculation of $\rho(\epsilon)$ has recieved some attention (Shklovskii and Efros 1980; Hearn, McInnes and Butcher 1982, Cox 1982) only its qualitative features are well understood. It is reasonable to assume that $\rho(\epsilon)$ is sharply peaked at $\epsilon = 0$. Furthermore Shklovskii (1973) estimates the value of the Fermi energy at $T = 0$. He finds

$$\mu^*(T=0) = \epsilon_F = 0.99 \frac{e^2 N_D^{1/3}}{4\pi\epsilon\epsilon_0} (1 - 0.3K^{1/4}) \qquad (7.3.3)$$

when K, the compensation ratio, is small. This value would be the activation energy in an R-hopping approach; for the parameter values of the silicon sample under consideration we find $\epsilon_F = 7.7$ meV. We now select a one-parameter function for $\rho(\epsilon)$ and use equation (7.2.3) to fix that parameter. To be definite we use a Gaussian distribution:

$$\rho(\epsilon) = \frac{N_D}{\Delta(2\pi)^{1/2}} \exp\left[\frac{-\epsilon^2}{2\Delta^2}\right] \qquad (7.3.4)$$

and determine Δ from

$$\int_{-\infty}^{\epsilon_F} \rho(\epsilon)d\epsilon = n \qquad (7.3.5)$$

which yields $\Delta = 2.8$ meV.

The parameters needed to evaluate R_0 in equation (1.2)

are known so that there are now no adjustable parameters in the theory. Adopting the paramter values $\alpha^{-1} = 2.1\ 10^{-9}$m; $\alpha'^{-1} = 9.3\ 10^{-10}$m; $n_m = 6$; $\nu = 3/2$ (Miller and Abrahams 1960) and $E_1 = 6$ eV; $\epsilon = 11.7$; $\rho_0 = 2.3\ 10^4$ kg m^{-3}; $V_s = 9\ 10^3 ms^{-1}$ (Hayden 1978) we obtain $R_0 = 6.8\ 10^{10} T\ s^{-1}$. For simplicity κ was set equal to its high temperature value of 2.7. The determination of $\mu^*(T)$ and the solution of the EPA equations was performed numerically. A great economy of computer time without much loss of accuracy was obtained by using the analytic approximations to the r-integrals in equations (6.2.4) and (6.2.5), detailed in Appendix A.
The results are plotted as full lines in figs. 11 and 12. The theory accurately reproduces the transitions from a.c. to d.c. behaviour and from activated to weak temperature dependence in the a.c. conductivty that are observed. At low temperatures the magnitude of the a.c. conductivity is proportional to $[\rho(\epsilon_F)]^2$. Within the constraint of equation (7.2.3) the value of $\rho(\epsilon_F)$ is sensitive to the shape of $\rho(\epsilon)$ and we can attribute the scale discrepency in the a.c. conductivity to the somewhat arbitrary choice of a Gaussian density of states. In all other respects the theory is in very good agreement with the data and this is a satisfying result considering the simplicity of the model assumptions and the fact that there are no adjustable parameters in the theory.

7.4 Impurity Conduction in n-GaAs

Kahlert et. al. (1976a,b) have measured the dependences of d.c. conductivity on donor concentration and temperature and a.c. conductivity on donor concentration and frequency in compensated n-type gallium arsenide. Results for three

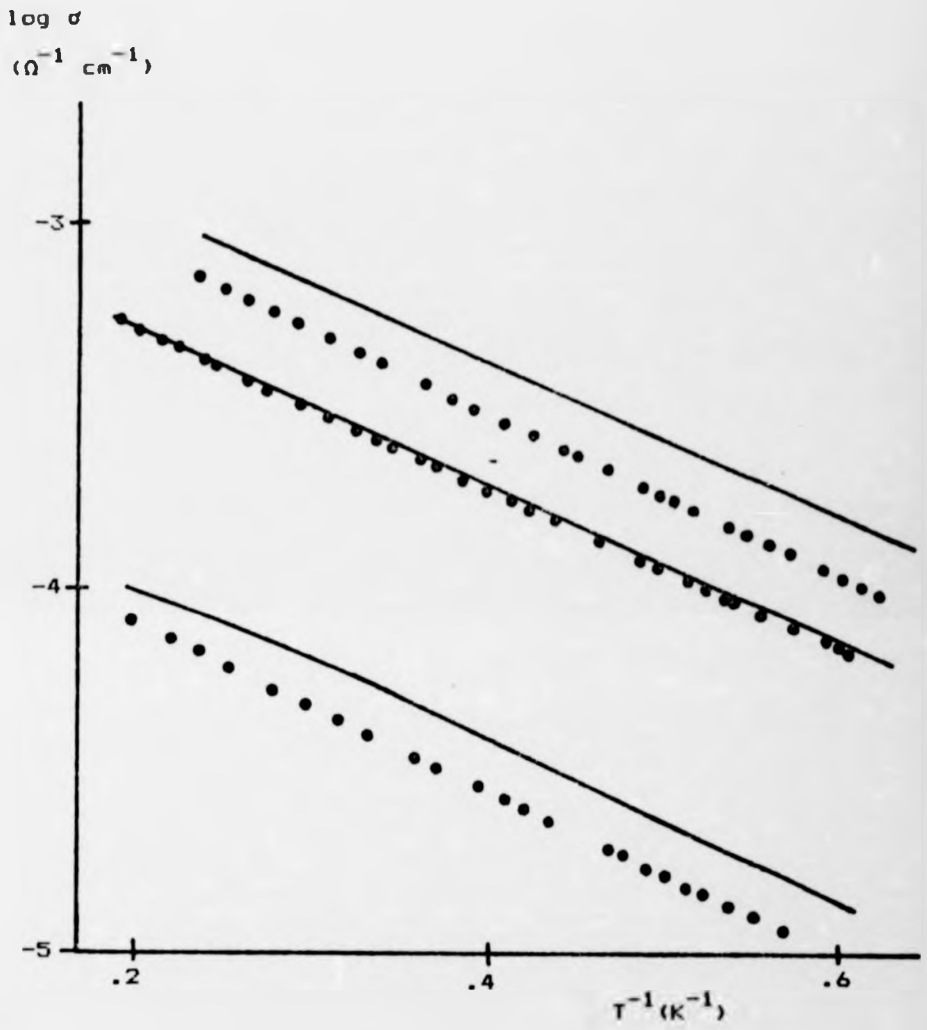


FIGURE 13

Comparison with impurity conduction in n-GaAs: conductivity vs inverse temperature at various donor concentrations. The three sets of points are the experimental data of Kahlert et. al. (1976b). The curves, corresponding to each set of points in ascending order, are from the calculations of the EPA.

samples are presented with donor concentrations N_D = 1.35, 1.9 and 2.1 $10^{17}cm^{-3}$ and corresponding compensation ratios of 0.7, 0.62 and 0.53 respectively. The d.c. conductivity is activated. Kahlert analyses the data on the basis of an R-hopping approach, he uses the Scher and Lax theory; we have shown above that this is not a reliable approach. In section 7.2 we outlined our reasons for not using the R-hopping formalism described therein. The values of compensation ratio imply that ϵ_F lies close to mid-band so that, with reference to the discussion in section 7.2, the source of activation must be hopping in band of width W such that $k_BT < W < k_BTs_p^{-}$. In contrast to the case of a peaked density of states with the Fermi level in the tail, the R-hopping model is not even well-defined for the a.c. conductivity. In the calculation of Hayden and Butcher (1978) the activated behaviour comes about because they obtain the result $s_p = s_p^{-} + \beta\epsilon_3$, where ϵ_3 is some fraction of W, rather than g_a containing the activation factor.

Very little information is available on the density of states in this case other than the fact that, since the compensation is not small, $\rho(\epsilon)$ is expected to be rather broad. We therefore adopt the simplest approach and take $\rho(\epsilon)$ to be rectangular, treating the width as an adjustable parameter. with

$$\rho(\epsilon) = \begin{cases} N_D/W & 0 \leq \epsilon \leq W \\ 0 & \text{Otherwise} \end{cases} \qquad (7.4.1)$$

equation (7.2.3) can be solved analytically giving

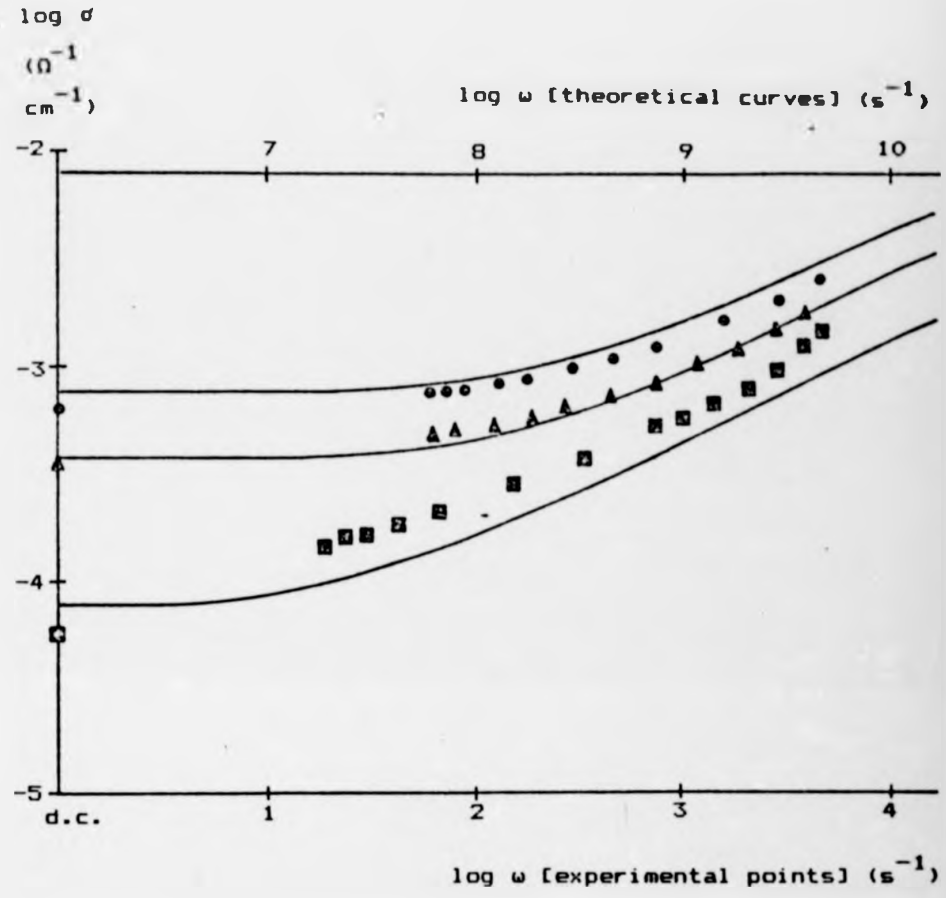


FIGURE 14

Comparison with impurity conduction in n-GaAs: conductivity vs angular frequency for various donor concentrations. The sets of data points, in the lower frequency scale, are the experimental data taken from Kahlert (1976a). The corresponding curves of the EPA have the upper frequency scale.

$$\mu^{*} = \frac{1}{\beta} \ln \left[\frac{\exp(\beta W n/N_D) - 1}{1 - \exp[\beta w(n/N_D) - 1]} \right] \qquad (7.4.2)$$

Putting $\kappa = 2.7$, $\nu = 2$ and $R_0 = 2.6\times10^{12}T$ (Kahlert et. al. 1976b) we have solved the EPA equations numerically, again using the analytic approximations detailed in appendix A. With W = 1.7 meV we have found that the activation energy of the d.c. conductivity is accurately reproduced. The results are plotted in fig. 13 showing that the agreement obtained is qualitatively and quantitatively very good. The a.c. conductivity comparison in fig. 14 shows that whereas the theory reproduces the qualitative features of the data the onset of a.c. conductivity occurs at a frequency which is six orders of magnitude higher than that observed. There are no parameters that could be adjusted to correct this discrepency. Equation (7.4.1) is consistent with the available information and the EPA is verified as an accurate solution of the rate equations. A question is therefore raised concerning ther validity of the approximations inherent in the rate equation approach itself with respect to the description of a.c. conductivity in this situation.

7.5 Hopping Conductivity in Amorphous Germanium

The Miller-Abrahams rate equation model is specifically developed for impurity conduction. Nevertheless it has been applied to conduction in amorphous semiconductors at low temperatures. The justification is that the two systems share the common feature that transport in localised states is responsible for the conductivity. Furthermore the probable complexity of the electron states and their

interactions with the lattice vibrational modes has inhibited the developement of a tractable and more realistic model. The application of the rate equation theory as it stands is accomplished by treating R_0, α and $\rho(\epsilon)$ as adjustable parameters. It then remains to be seen whether the theory can describe the qualitative features of the data and whether quantitative agreement can be obtained with reasonable parameter values. We have made a quantitative comparison of the EPA with data obtained by Long and Balkan (1979) for amorphous Germanium. We choose $\alpha^{-1} = 1.4\ 10^{-9}$m (Gilbert and Adkins 1976) and put $\nu = 2$ because the system is isotropic. The $T^{1/4}$ d.c. conductivity behaviour observed is consistent with the assumption of a very wide flat density of states curve (Mott and Davis 1979) so we put $\rho(\epsilon) = \rho(\epsilon_F)$. Both the bandwidth and the value of μ^* are then irrelevent at low temperatures and we put $\mu^* = 0$. To simplify the calculations we approximate the energy dependence of $g(\epsilon_1,\epsilon_2,r)$ acccording to the work of Ambegaokar et. al. (1971) and put

$$g(\epsilon_1,\epsilon_2,r) = \frac{e^2R_0}{k_BT}(\alpha r)^2\exp(-2\alpha r - [|\epsilon_1| + |\epsilon_2| + |\epsilon_1 - \epsilon_2|]/2k_BT) \qquad (7.5.1)$$

McInnes (1982) has shown that for low temperatures there is little difference between d.c. conductivities obtained numerically using equation (7.5.1) or the full expression (2.3.2) with (1.2). Furthermore in the last chapter we were able to find the value of κ appropriate to this type of energy dependence and obtained $\kappa = 4.4$. The EPA equations are solved numerically and we find that the theory

reproduces the correct exponential dependence of the d.c. conductivity on $T^{-1/4}$ with $24\alpha^3/n\rho(\epsilon_F)k_B = 1.22\times10^8$ K and $R_0 = 4.6\times10^{19}T\ s^{-1}$. The calculated a.c. conductivity with these parameters is plotted in fig. 15 together with the experimental data for two temperatures. The theory reproduces the ω^s dependence of $\sigma(\omega)$ and the weakening of its temperature dependence as ω increases. However, the onset of a.c. behaviour is predicted to occur at a frequency two orders of magnitude higher than that observed. Values of R_0 in the range we have found have been observed in comparisons of this type (Butcher and Hayden 1977b) and are very hard to understand as a physical frequency in contrast to the values found in impurity conduction which can easily be interpreted as a characteristic phonon frequency.

The same data has previously been analysed by Movaghar et. al. (1980c) who demonstrated complete agreement but with some additional fitting. The availability to us of the raw experimental data (Long 1980) enabled us to check their results. We found similar results to ours except with $R_0 \sim 10^{27}$. The difference between this value and ours has two origins. Firstly they used the "barrier approximation" scheme and in the last chapter we showed that this underestimates the conductivity and secondly they put $\nu = 0$. The second point is of interest; including the factor $(\alpha r)^2$ in equation (7.5.1) reduces the value of R_0 required by three orders of magnitude. It would therefore not be unreasonable to suppose that with a better approximation to the transistion rate the theory might describe this data with physically realistic parameter

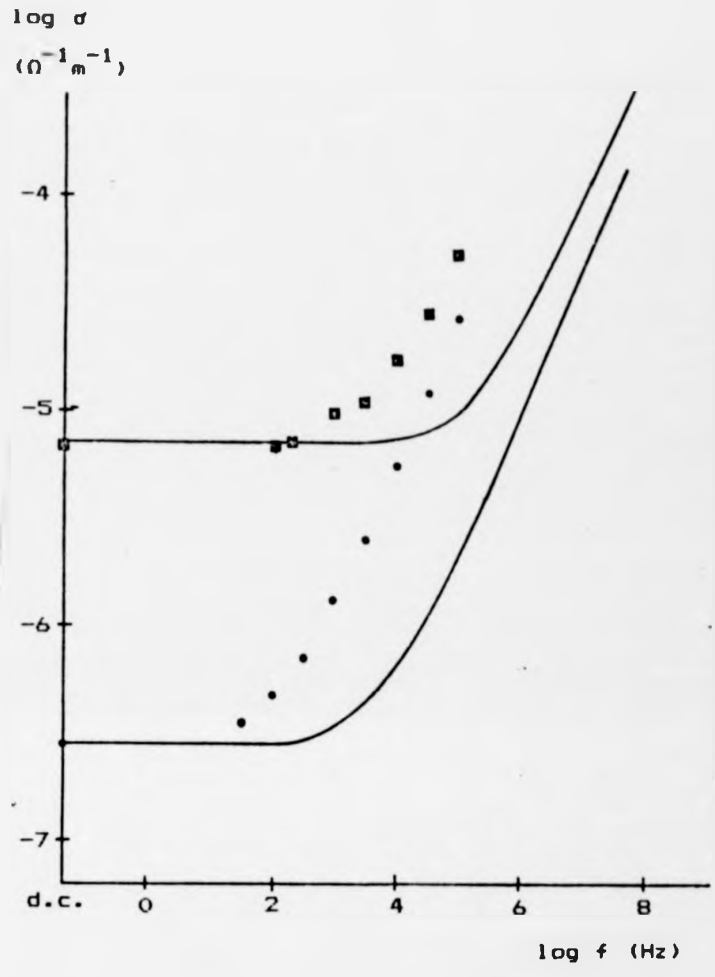


FIGURE 15

Comparison with conduction in amorphous germanium: conductivity vs frequency f at two temperatures. The circles and squares represent the data of Long and Balkan (1979) for 77K and 102K respectively. The upper and lower curves are the results of the EPA.

values.

7.6 Discussion

Our investigation of impurity conduction in two types of systems shows that the rate equation model provides a good description of the d.c. conductivity in both cases. The difference in the comparison of a.c. conductivities is then quite startling. We should therefore consider what the differences are between the two systems. The density of donors measured on the scale $N_D a^{-3}$ is similar. The main differences are the nature of the material and the compensation ratio. The former difference may be of some consequence as GaAs is piezoelectric; the Miller-Abrahams rates may not be appropriate (Kahlert et. al. 1976b). The effect of the higher compensation ratio in the GaAs samples and the subsequent increase in carrier density may have consequences regarding the neglect of Coulomb interactions and local field corrections in the theory. It is difficult to see why these factors should only affect a.c. conductivity. Further theoretical work, beyond the scope of this thesis, should lead to a more general theory incorporating these effects. Further experimental investigations are needed to identify precisely the conditions under which the present theory fails.

There are many differences between amorphous semiconductors and impurity bands. The nature of the electron and phonon states and the transition rates are examples; the list is easily extended. In view of this the application of the rate equations to conduction in amorphous semiconductors might seem inappropriate. The common concept of thermally activated transport among

localised states is however apparently sufficient to allow the theory success in a qualitative description. Our results show this and also show that the theory is not a valid quantitative model; the need for a characteristic frequency of 10^{21}Hz is sufficient indictment. The rate equations can only be viewed as a first approximation to the situation in an amorphous semiconductor; future theoretical investigations will hopefully lead to a more realistic theory.

CHAPTER 8 - UNIFIED THEORY OF THE AC AND DC HALL EFFECT

8.1 The Rate Equations for the Hopping System in a Magnetic Field

We consider the low-field Hall effect in the disordered hopping system and suppose that an a.c. electric field $E \exp(-i\omega t)$ is applied in the x-direction in the presence of a constant, uniform magnetic field B in the z-direction. We then seek to evaluate the current flowing in the y-direction, J_y, in terms of which the Hall mobility μ_H is defined by $\mu_H = -J_y/BJ_x$; J_x is evaluated to zeroth order in B and J_y to first order. Since they are macroscopic quantities they may be replaced by their configuration averages. Now $\langle J_x \rangle = \langle \sigma(\omega) \rangle E$ and the evaluation of $\sigma(\omega)$ has already been discussed. To evaluate $\langle J_y \rangle$ we need to know the perturbation of the transition rate R_{mn} to first order in B. This problem was first discussed by Holstein (1961) who assumed that the primary effect of the magnetic field is to introduce a phase factor into the transition amplitude which determines R_{mn}. The phase factor cancels out of the direct hop rate between sites m and n. However, a linear perturbation of R_{mn} results when we consider the interference term between a direct process and a process which proceeds via an arbitrary intermediate site p. The transition rate is now

$$R'_{mn} = R_{mn} + \sum_p R^H_{mpn} \qquad (8.1.1)$$

R^H_{mpn} was originally calculated by Holstein for conditions of thermal equilibrium, in a non-degenerate formalism. Boettger and Bryksin (1977) and Aldea and Banyai (1978) have

extended the formalism to degenerate electron statistics. They then put

$$R^{H}_{mpn} = (1 - f_p)R^{e}_{mpn} + f_p R^{h}_{npm} \qquad (8.1.2)$$

where R^{e}_{mpn} is the transition rate for an electron hopping from site m to site n when site p is empty and R^{h}_{npm} is the rate for a hole hopping from site n to site m when site p is full.

In chapter 2 we made the assumption that the effect of the external ~~electric~~ electric field is contained in replacing ϵ_m in the transition rates by $\epsilon_m + U_m$ and expanded to first order in U_m. We also assumed that detailed balance holds and were then able to linearise the rate equations. Equivalent to equations (2.1.2) and (2.1.3) are the relations

$$R^{0}_{mn} = \exp(\beta\epsilon_m)T_{mn} \qquad (8.1.3)$$

and

$$R_{mn} = \exp(\beta\epsilon_m)T_{mn}(1 + \beta U_m) \qquad (8.1.4)$$

where T_{mn} is symmetrical under interchange of the subscripts m and n. Boettger and Bryksin obtain the symmetry properties of the three-site contibutions to R'_{mn} and these lead us to write

$$R^{e}_{mpn} = \exp(\beta\epsilon_m)A^{e}_{mpn}(1 + \beta U_m) \qquad (8.1.5a)$$

$$R^{h}_{npm} = \exp(-\beta\epsilon_n)A^{h}_{npm}(1 - \beta U_n) \qquad (8.1.5b)$$

where $A^{(e,h)}_{mpn}$ are antisymmetric under subscript permutations.It therefore follows that $R^{(e,h)}_{mpn}$ are

antisymmetric under interchange of the subscipts p and n. When equations (8.1.1) and (8.1.2) are substituted into equations (1.1) and this property is employed, we obtain the required rate equations:

$$\frac{df_m}{dt} = \sum_n [f_n(1 - f_m)R_{nm} - f_m(1 - f_n)R_{mn}] + \sum_{np} [f_n(1 - f_m)(1 - f_p)R^e_{npm} - f_m(1 - f_n)f_p R^h_{npm}] \quad (8.1.6)$$

Aldea and Banyai, who generalise Holstein's work, obtain explicit expressions for A^e_{mpn} and A^h_{mpn} which are written in terms of T_{mn} and a tunnelling integral t_{mn}, defined such that the equilibrium two-site rate is

$$R^0_{mn} = [R_0/t_0^2]\, F(\epsilon_m, \epsilon_n)\, t_{mn} \quad (8.1.7)$$

where

$$t_{mn} = t_0 \exp[-p(r)/2]$$

and where, in Miller-Abrahams rate (1.2) for example,

$$p(r) = 2\alpha r - v\ln\alpha r$$

and

$$F(\epsilon_m, \epsilon_n) = \frac{\beta(\epsilon_m - \epsilon_n)}{\exp[\beta(\epsilon_m - \epsilon_n)] - 1}$$

The results are

$$A^e_{npm} = \frac{-e\underline{B}.\underline{r}_{np}\hat{\wedge}\underline{r}_{mp}}{8t_{mn}t_{mp}t_{pn}}[\, T_{np}T_{pm}t^2_{nm}\exp(\beta\epsilon_p) + \text{cyclic permutations}] \quad (8.1.8a)$$

and

$$A^{h}_{npm} = \frac{-e\underline{B}.\underline{r}_{np}\hat{}\underline{r}_{mp}}{8t_{mn}t_{mp}t_{pn}} \exp[-\beta(\epsilon_n + \epsilon_p + \epsilon_m)] \; [\; T_{np}T_{pm}t^{2}_{nm} + c.p.] \tag{8.1.8b}$$

8.2 Linearisation and Formal Solution

We linearise equations (8.1.6), adopting the notation of section 2.3 and generalising the formalism of Butcher and Kumar (1980). Upon putting

$$f_m = f^{0}_{m} + \beta f^{0}_{m}(1 - f^{0}_{m})\Phi_m$$

and noting that, with f^{0}_{m} given by equation (2.1.1),

$$1 - f^{0}_{m} = \exp(\beta\epsilon_m)f^{0}_{m}$$

we find that substitution of equations (8.1.4) and (8.1.5) into equation (8.1.6) and some straightforward but tedious manipulation, that uses the symmetry properties of the $A^{(e,h)}_{npm}$ and T_{mn} and retains only terms linear in U_m and Φ_m, yields

$$C_m \frac{d}{dt}(V_m + e^{-1}U_m) = \sum_n g_{nm}(V_n - V_m) - \sum_{np}\sum g^{H}_{npm}V_n \tag{8.2.1}$$

where C_m, V_m and g_{mn} are defined in section 2.3 and

$$g^{H}_{npm} = -e^{2}\beta f^{0}_{n}f^{0}_{p}f^{0}_{m}(\exp[\beta(\epsilon_n + \epsilon_p + \epsilon_m)]A^{e}_{npm} + A^{h}_{npm}) \tag{8.2.2}$$

which is antisymmetric under suffix permutations. If we

assume a time dependence of the form $\exp(-i\omega t)$ for V_m we can rewrite eqn. (8.2.1) as

$$-i\omega C(\underline{V} + E\underline{x}) = g\underline{V} + g^H\underline{V} \tag{8.2.3}$$

where we have adopted a matrix notation in which $\underline{V}$ and $\underline{x}$ are column matrices with elements V_m and x_m respectively and C, g and g^H are matrices whose elements are given by

$$C_{mn} = C_m\delta_{mn}$$

$$g_{mn} = -\delta_{mn}\sum_p g_{mp} + (1 - \delta_{mn})g_{mn}$$

and

$$g^H_{mn} = -\sum_p g^H_{npm} \tag{8.2.4}$$

respectively. We then find that

$$\underline{V} = -G(i\omega CE\underline{x} + g^H\underline{V}) \tag{8.2.5}$$

where $G = (g + i\omega C)^{-1}$. Since we seek a solution to $\underline{V}$ which is linear in B, we iterate once upon equation (8.2.5) and find

$$\underline{V} = \underline{V}^x - Gg^H\underline{V}^x \tag{8.2.5}$$

where $\underline{V} = -Gi\omega CE\underline{x}$ is the voltage vector for $\underline{B} = \underline{0}$ and $\underline{E}$ parallel to the x-axis. We seek to evaluate J_y which is, by analogy with equation (2.2.4) given by

$$J_y = -\frac{i\omega}{\Omega}\sum_n y_n C_n(V_n + E\,x_n)$$

$$= -\frac{i\omega}{\Omega}\,\tilde{\underline{Y}}\,C\,(\underline{V} + E\underline{x})$$

$$= -\frac{i\omega}{\Omega}\,\tilde{\underline{Y}}\,C\,(\underline{V}^x - Gg^H\underline{V}^x + E\underline{x})$$

the terms in the last line which do not invlove g^H give J_y when $\underline{B} = \underline{0}$ and hence vanish in the thermodynamic limit because of macroscopic isotropy. Hence

$$J_y = \frac{i\omega}{\Omega}\,\tilde{\underline{Y}}\,C\,G\,g^H\,\underline{V}^x$$

Now $\underline{V}^y = -Gi\omega CE\underline{y}$ is the voltage vector for $\underline{B} = \underline{0}$ and $\underline{E}$ parallel to the y-axis and $\tilde{\underline{V}}^y = -i\omega E\underline{y}\tilde{C}G$ since C and g , and hence G, are symmetric. We then have

$$J = \frac{-1}{\Omega E}\,\tilde{\underline{V}}^y\,g^H\,\underline{V}^x$$

$$= \frac{-1}{\Omega E}\sum_{mn}\sum g^H_{mn}V^x_m V^y_n \qquad (8.2.6)$$

We see that J_y is a weighted sum of products of site voltages calculated when $\underline{B} = \underline{0}$. By substituting for g^H_{mn} from equation (8.2.4) and making repeated use of the antisymmetry properties of g^H_{mpn} we may rewrite equation (8.2.6) in the more convenient form

$$J_y = \frac{-1}{6\Omega E}\sum_{mnp}\sum\sum g^H_{npm}(V^x_{mp}V^y_{pn} - V^y_{mp}V^x_{pn})$$

$$= \frac{-1}{6\Omega E}\sum_{mnp}\sum\sum g^H_{npm}(\underline{V}_{mp}\hat{}\,\underline{V}_{pn})_z \qquad (8.2.7)$$

In the second line we have recognised the second factor in the summand as the vector product of the three-dimensional

vectors:

$$\underline{V}_{mn} = (V^x_{mn}, V^y_{mn}, V^z_{mn})$$

$$= (V^x_m - V^x_n , V^y_m - V^y_n , V^z_m - V^z_n)$$

where V^z_m is defined, by analogy with V^x_m and V^y_m, as the voltage at site m when $\underline{B} = \underline{0}$ and $\underline{E}$ is parallel to the z-axis.

Equation (8.2.7) is our main result. In order to find an explicit expression for the configuration averaged Hall mobility $\langle \mu^H(\omega) \rangle$, we notice that g^H_{npm} in equation (8.2.2) with B in the z-direction, may be written as

$$g^H_{npm} = -\frac{1}{2}(y_{np}x_{pm} - x_{np}y_{pm})Bg^{-H}_{npm} \qquad (8.2.8)$$

where g^{-H}_{npm} depends only on the energies of the sites n,p and m and their spatial separations. Now the vector area of the triangle bounded by sites n,p and m is

$$\underline{A}_{npm} = -\frac{1}{2}\underline{r}_{np} \wedge \underline{r}_{pn}$$

so that, upon taking the configuration average of equation (8.2.7), dividing by $\langle \sigma(\omega) \rangle E$, adding results with $\underline{B}$ in the x, y and z-directions and dividing by 3, we finally obtain

$$\mu^H(\omega) = \frac{1}{18\langle \sigma(\omega) \rangle E^2} \int \rho(\epsilon_m)d\epsilon_m \int \rho(\epsilon_n)d\epsilon_n \int \rho(\epsilon_p)d\epsilon_p \ldots$$

$$\ldots \int d\underline{r}_{mn} \int d\underline{r}_{mp}\, g^{-H}_{mpn}\, \underline{A}_{npm} \cdot \langle \underline{V}_{nm} \wedge \underline{V}_{mp} \rangle' \qquad (8.2.9)$$

The quantity $\langle \underline{V}_{nm} \wedge \underline{V}_{mp} \rangle'$ is the vector product of the voltage drop vectors averaged over all site separations and energies in the system except those pertaining to the

triangle of sites m,n and p. In the next section we find an approximation to it and calculate $\langle \mu^H(\omega) \rangle$.

8.3 The Extended Three-Site Approximation

In the last section we showed that the Hall mobility is completely determined when we know the mean of a vector product of voltage drops between an arbitrary three sites in the system. Because the voltages are to be calculated with $\underline{B} = \underline{0}$, the equivalent circuit is identical to that considered in chapter 6 and the type of approach that we used there for the calculation of $\langle \sigma(\omega) \rangle$ is immediately applicable.

Let us label the three arbitrary sites as 0,1 and 2. If we ignore the effect of the external circuit on the voltages at these sites and solve Kirchhoff's equations for the voltages on the sites with the E-field in the x,y, and z-directions, we can obtain a three-site approximation to the Hall mobility. This is analogous to the pair approximation to the conductivity. Holstein used this approximation to discuss the a.c. Hall mobility for the case of non-degenerate electron statistics. We can easily extend his result to the general case by solving equation (8.2.1) with $\underline{B} = \underline{0}$ and m,n = 0,1,2. However, just as the pair approximation to the conductivity gave a null result in the d.c. limit, so too does the three-site approximation to the Hall mobility. To obtain a non-zero value for $\mu^H(0)$ the circuit external to the sites 0,1 and 2 must be taken into account. We now adopt the analogous procedure to that used in chapter 6 for the derivation of the EPA to $\sigma(\omega)$ and represent the external circuit by elements averaged over all site coordinates except for ϵ_0, ϵ_1 and ϵ_2. We immeditely

obtain the equivalent circuit for the extended three site approximation; this is shown in fig. 16. We recall from chapter 6 that Y_i is a function only of ϵ_i and that the external generators are given by $e_i = -Ex_i$. The definition of Y_i is the same here as in chapter 6 , namely that it is the average admittance of the rest of the circuit to current flowing out of a site with energy ϵ_i and the equation derived there for Y_i may be used here. It then remains to find the required vectors of voltage drops for substitution into equation (8.2.9) and this is straightforward.

Kirchoff's equations for the voltages at the sites 0,1 and 2 may be conveniently written in the matrix form:

$$K \begin{bmatrix} V_0 \\ V_1 \\ V_2 \end{bmatrix} = \begin{bmatrix} U_0 \\ U_1 \\ U_2 \end{bmatrix} \qquad (8.3.1)$$

where

$$K_{ij} = K_{ji} = -g_{ij} \qquad i \neq j$$
$$= P_i + \sum_{j \neq i} g_{ij} \qquad i = j$$

$i = 0,1,2$ and

$$P_i = Y_i - i\omega C_i$$

and

$$U_i = -E\gamma_i P_i$$

with $\gamma = x,y,z$. If $X = K^{-1}$ we then have

$$V_i = \sum_j X_{ij} U_j \qquad (8.3.2)$$

The distinct matrix elements of X are:

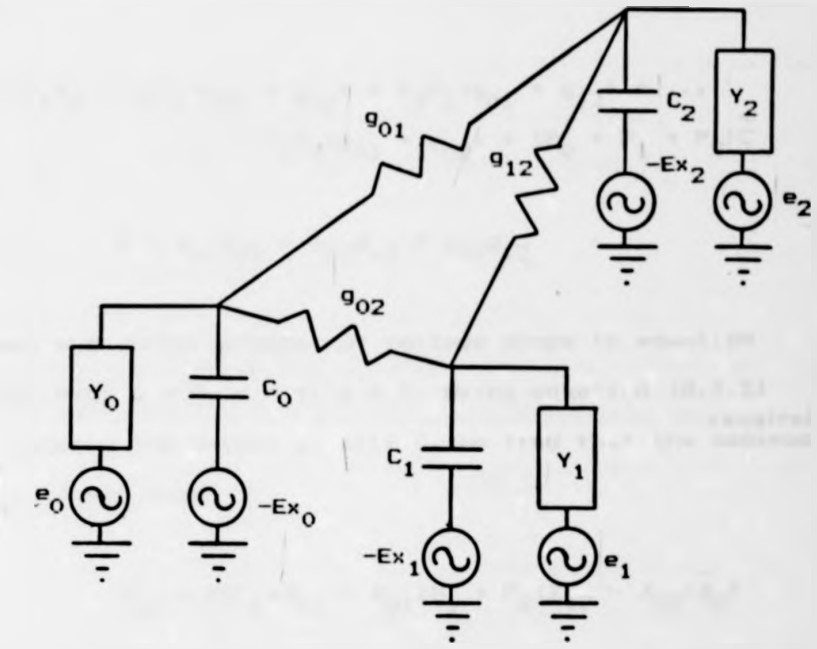


FIGURE 16

The equivalent circuit for the extended three site approximation.

$$\Delta X_{00} = P_1P_2 + P_1(g_{02} + g_{12}) + P_2(g_{01} + g_{12}) + \tilde{C}$$

$$\Delta X_{11} = P_0P_2 + P_0(g_{02} + g_{12}) + P_2(g_{01} + g_{02}) + \tilde{C}$$

$$\Delta X_{22} = P_0P_1 + P_0(g_{01} + g_{12}) + P_1(g_{01} + g_{02}) + \tilde{C}$$

$$\Delta X_{ij} = g_{ij}P_k + \tilde{C} \qquad i \neq j;\ k \neq i,j \tag{8.3.3}$$

where

$$\Delta = P_0P_1P_2 + P_0P_1(g_{12} + g_{02}) + P_0P_2(g_{01} + g_{12}) + \ldots$$
$$\ldots + P_1P_2(g_{01} + g_{02}) + (P_0 + P_1 + P_2)\tilde{C}$$

and

$$\tilde{C} = g_{01}g_{02} + g_{01}g_{12} + g_{02}g_{12}$$

We seek the vector product of voltage drops in equation (8.2.9) with m = 0, n = 1, p = 2. Using equation (8.3.2) and choosing the origin at site 0, we find that the required voltage drops are:

$$\underline{v}_{10}^{\delta} = E[P_1(X_{11} - X_{01})\hat{\underline{\delta}}_1 + P_2(X_{12} - X_{02})\hat{\underline{\delta}}_2]$$

$$\underline{v}_{02}^{\delta} = E[P_1(X_{01} - X_{12})\hat{\underline{\delta}}_1 + P_2(X_{02} - X_{11})\hat{\underline{\delta}}_2]$$

where $\hat{\underline{\delta}}_i$ is δ_i multiplied by a unit vector in the i-direction. Using equation (8.3.3) we obtain:

$$\underline{v}_{10} \wedge \underline{v}_{02} = E^2 \underline{r}_{10} \wedge \underline{r}_{02} P_0P_1P_2/D \tag{8.3.4}$$

and the final result for the Hall mobility at frequency ω is

$$\mu^H(\omega) = \frac{1}{9<\sigma(\omega)>} \int \rho(\epsilon_m)d\epsilon_m \int \rho(\epsilon_n)d\epsilon_n \int \rho(\epsilon_p)d\epsilon_p \ldots$$

$$\ldots \int_0^\infty 4\pi r_1^2 dr_1 \int_0^\infty 4\pi r_2^2 dr_2 \int_{-1}^{1} d(\cos\theta)\ A_{102}^2 \bar{g}_{102}^H P_0 P_1 P_2 / \Delta \qquad (8.3.5)$$

where $r_1 = r_{01}$; $r_2 = r_{02}$; $r_3 = r_{12} = (r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta)^{1/2}$ and $A_{102}^2 = r_1^2 r_2^2 \sin\theta$ /4 and the integrand is a function of ϵ_0, ϵ_1, ϵ_2, r_1, r_2, and r_3. In the next section we give the results of numerical evaluations of the integrals in equation (8.3.5) for a number of special cases.

8.4 Results and Discussion

We present graphical results for $\mu^H(\omega)$ at all frequencies for the R-hopping model and at $\omega = 0$ for an energy dependent model. Computer simulation data has recently become available for both models at $\omega = 0$ (Butcher and McInnes 1981, McInnes 1982b).

The d.c. Hall mobility has also been calculated by a number of other authors using a variety of approaches. Boettger and Bryksin (1977), Friedman and Pollak (1978) and Butcher and Kumar (1980) use percolation theory to find $\mu^H(0)$ for R-hopping systems. Butcher and McInnes (1981) improve the method of Butcher and Kumar. The various approaches differ in the way that the configuration average is dealt with; the details need not concern us here. Friedman and Pollak (1981) and Grunewald et. al. (1982) obtain results for an energy dependent model when the conductivity follows the $T^{-1/4}$ law. The latters author's approach is an extension of the method used by Boettger and Bryksin. Movaghar, Pohlmann and Wuertz (1981, hereafter

referred to as MPW) extend the MRWA, described in chapters 4 and 5, to a theory of the Hall mobility by using a three-site decoupling of the Green's function. As in the comparison of the MRWA to the EPA, their results are similar to ours. In fact there result can be obtained by neglecting the terms

$$P_0P_2(g_{01} + g_{12}) + (P_0 + P_2)\tilde{C}$$

in Δ in equation (8.3.5). The difference does not have a great quantitative effect, as we demonstrate below, but it does mean that the integrand in the MPW theory is not properly symmetric in the three site indices whereas the extended three-site approximation is. Furthermore, although the bare three-site approximation has not been rigorously established as the low density asymptotic formula for $\mu^H(\omega)$ when $\omega \neq 0$ in the same way as the pair approximation to $\sigma(\omega)$ has been, we nevertheless would intuitively expect this to be so. Consequently the extended three-site approximation is expected to be more accurate in the limit $n_s \to 0$ when $\omega \neq 0$ than the MPW theory.

In their computer simulations, Butcher and McInnes used the forms

$$g_{mn} = g_a \exp(-2\alpha r_{mn}) \tag{8.4.1a}$$

and

$$g_{npm} = g_a^H (e/\hbar) \exp(-\alpha r_{npm}) \tag{8.4.1b}$$

where r_{npm} is the perimeter of the triangle with vertices at site n,p and m and g_a^H is a constant. These results follow when we set $\epsilon_m = \epsilon_p = \epsilon_n = 0$ in the transition rates and put $v = 0$. The ratio g_a/g_a^H is chosen to be 0.145. The integral

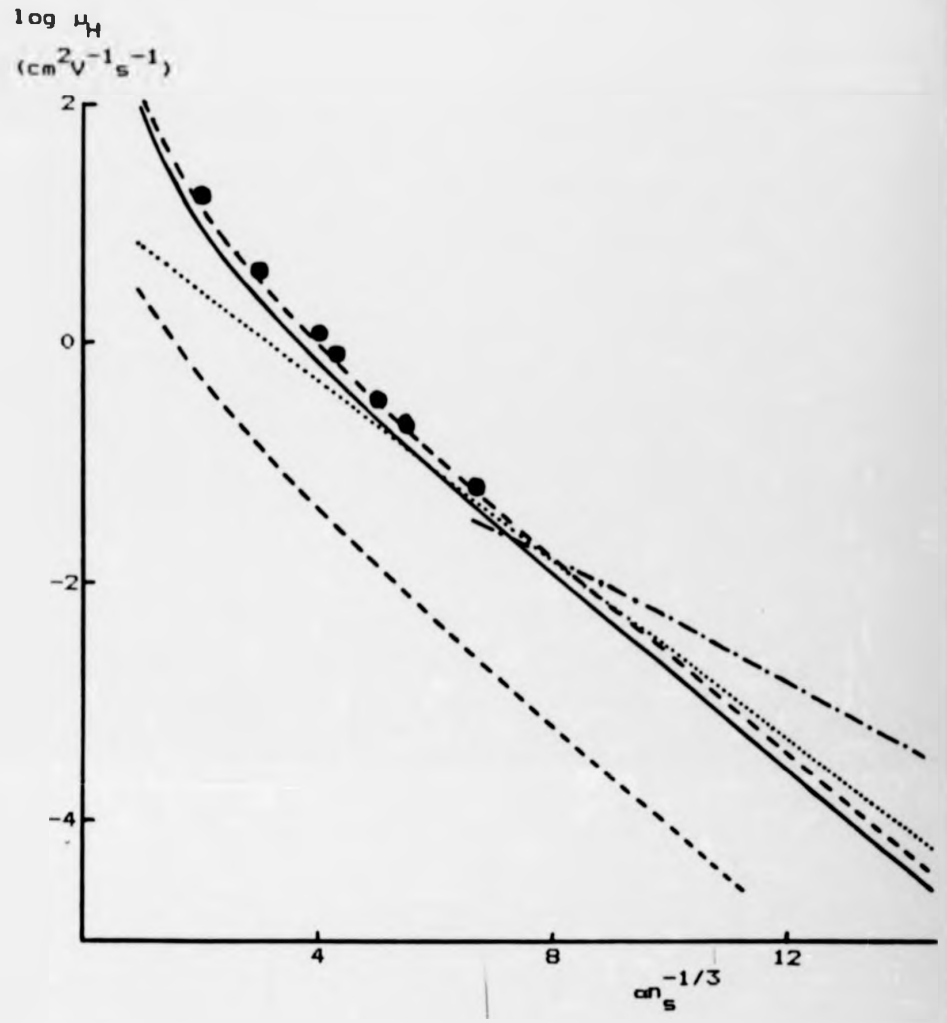


FIGURE 17

D.c. Hall mobility for the R-hopping system. The points are computer simulation data (Butcher and McInnes 1981). The full curve is the result from the extended three site approximation. The upper and lower dashed curves are the results from the theories of MPW and Boettger and Bryksin respectively. The dotted curve is the theory of Butcher and McInnes; the dashed-dot curve is the theory of Friedman and Pollak.

of the density of states in equation (8.3.5) is the site density and $\mu^H(0)$ is a function of $\alpha n_s^{-1/3}$. In fig. 17 we plot the results of a numerical evaluation of equation (8.3.5), with the definitions (8.4.1), and the computer simulation data. The agreement is very good. We also plot results of other theories; the MPW theory gives results which are quantitatively very similar to ours, the other theories show varying degrees of error.

McInnes (1982b) has recently obtained computer simulation data for the d.c. Hall mobility in an energy dependent model the parameters of which are the same as for his conductivity data that we compared with in chapter 6. He used transition rates that follow for the approximation scheme of Ambegaokar et. al. (1971) which puts

$$f_m^0 = \exp(-\beta[\epsilon_m + |\epsilon_m|]/2) \qquad (8.4.2a)$$

and

$$R_{mn}^0 = R_0 \exp(-2\alpha r_{mn} - \beta[|\epsilon_m + \epsilon_n| - \epsilon_m + \epsilon_n]/2) \qquad (8.4.2b)$$

Upon defining

$$\epsilon_{mn} = (|\epsilon_m| + |\epsilon_n| + |\epsilon_m - \epsilon_n|)/2 \qquad (8.4.3)$$

the two-site conductance is again given by

$$g_{mn} = g_0 \exp(-2\alpha r_{mn} - \beta\epsilon_{mn})$$

and the quantity $\bar{g}_{npm}^H$ in equation (8.3.5) becomes

$$\bar{g}_{npm}^H = g_a^H (e/\hbar) \exp(-\alpha r_{npm}) Q_{npm} \qquad (8.4.4)$$

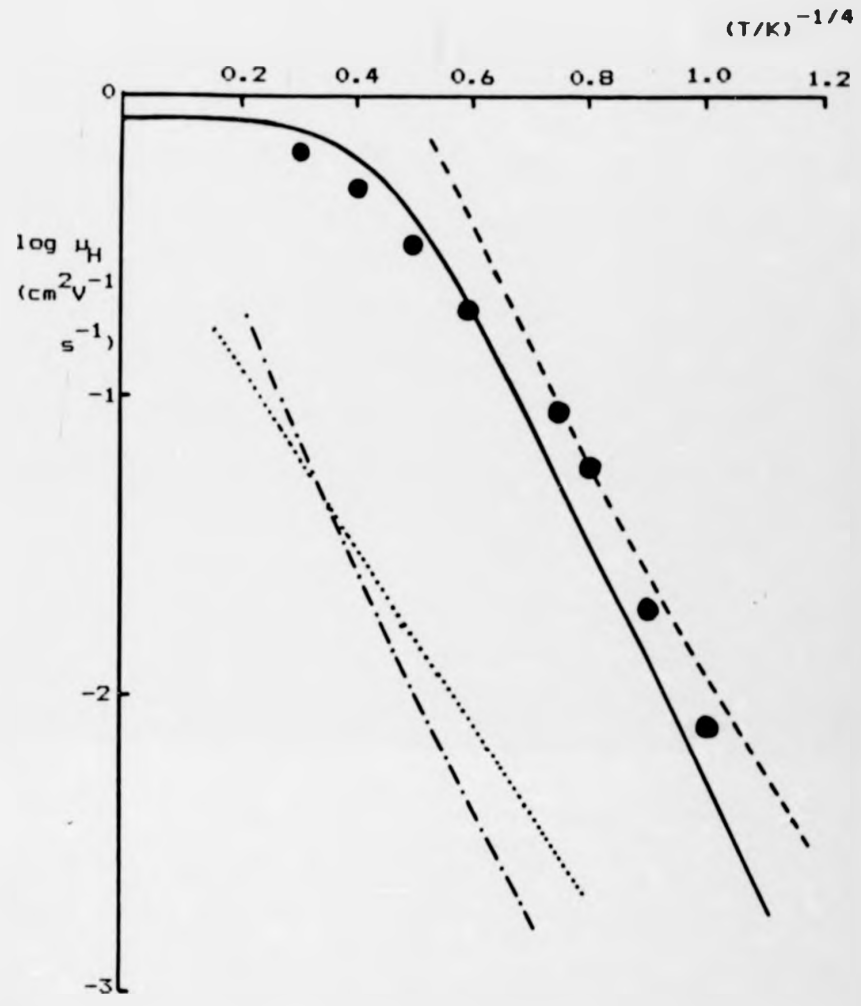


FIGURE 18

D.c. Hall mobility for the energy dependent model. The points are computer simulation data (McInnes 1982). The full curve is the result from the extended three site approximation. The other curves are taken from Gruenwald et. al. (1982) and represent the results of their percolation approach (dotted curve), their calculation of the energy dependent MPW theory (dashed curve) and the theory of Friedman and Pollak (dashed-dot curve).

where

$$Q_{npm} = [\exp(-\beta(\epsilon_{mm} + \epsilon_{np} - |\epsilon_p|)) + \text{cyclic permutations}]/3$$

Using these forms we have evaluated equation (8.3.5) numerically and effected a comparison with the data. the results are show in fig. 18 together with results of other theories. Our results are in good agreement with the data as is the extension of the MPW theory at low temperatures. The latter theory fails to show the saturation at high temperatures because it was calculated with an infinite bandwidth. The other theories show a significant error.

Although there is no data in the a.c. regime, we have nevertheless, for the sake of completeness, calculated the a.c. Hall mobility for the R-hopping model with $\nu = 0$. The results are plotted in fig. 19 and behave much as one would expect.

Amitay and Pollak (1966) attempted to measure the a.c Hall voltage, which is $B\mu^H/E$, at 10^5Hz. in impurity conduction in doped silicon and germanium. They failed to observe a Hall voltage above the noise level and hence any measurable Hall effect for hopping processes in these systems. Holstein (1961) had previously predicted a measurable value for the imaginary part of the Hall voltage at 10^5Hz. However he used an R-hopping, i.e high temperature, approximation. Amitay and Pollak notice this and, estimating the effect of finite T in Holstein's theory, they find that, within reasonable error limits, its prediction is in fact consistent with the null result they obtained experimentally. We expect that the extended three-site approximation will be similar to Holstein's bare three-site approximation at the frequency and density considered and that we can only regain

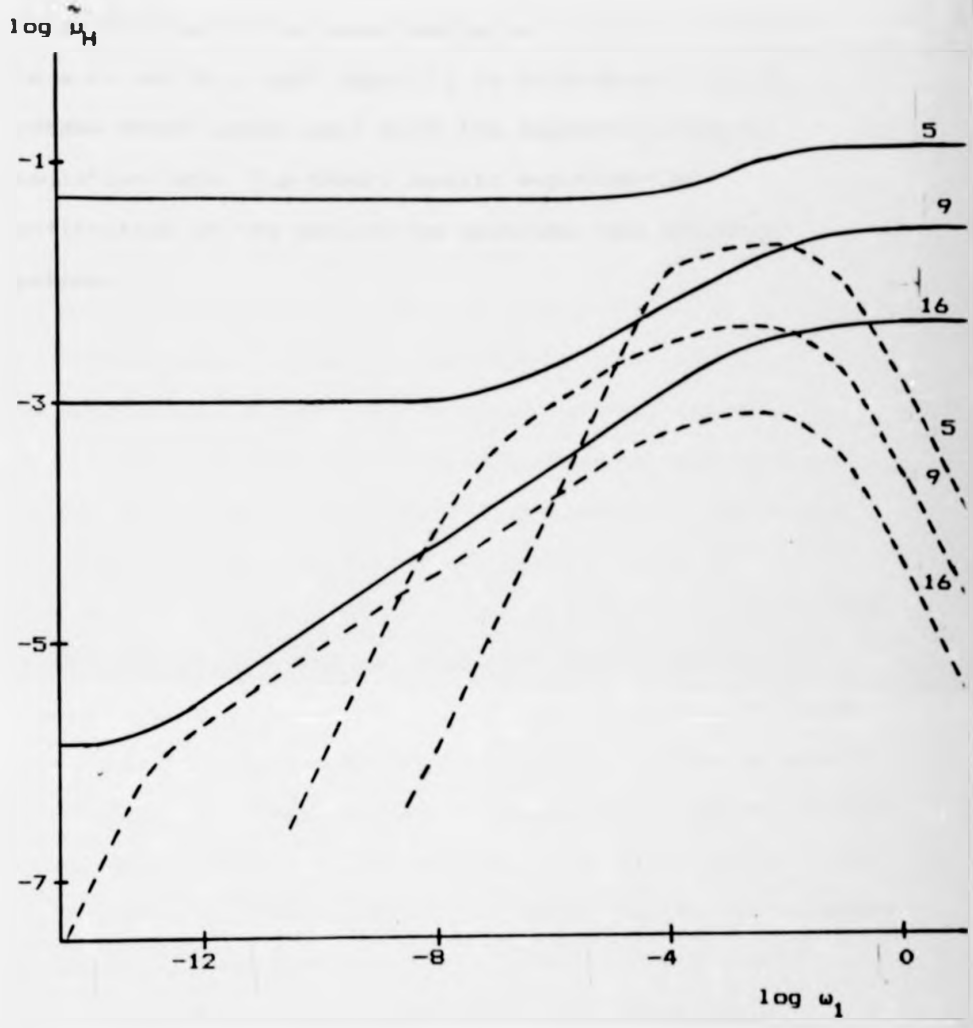


FIGURE 19

A.c Hall mobility for the R-hopping system. The full and dashed curves are the real and imaginary parts of the extended three site approximation to $\tilde{\mu}_H = \mu_H/\mu_0$, where $\mu_0 = (g_a^H/g_a)e/\hbar\alpha^2$, as a function of $\omega_1 = \omega/R_0$, for the values of $\alpha n_s^{-1/3}$ indicated.

this result by further analysis.

In conclusion, we have developed a general theory of the a.c. and d.c. Hall mobility in disordered hopping systems which agrees well with the available computer simulation data. The theory awaits experimental confirmation of its ability to describe real physical systems.

CHAPTER 9 - SUMMARY AND DISCUSSION

In this last chapter we survey the investigations undertaken in the previous chapters and identify some areas for future research.

We have discussed in detail the ~~developement~~ development of a unified theory of a.c. and d.c. hopping conductivity in both the random walk and equivalent circuit approaches. The latter approach proved to be more fruitful in that a simple analysis yields a conductivity formula that reproduces ,in the appropriate limits, all known asymptotic formulae and agrees well with data obtained from computer simulations. However the Green's function that one seeks in the random walk approach has some applications in considering phenomena other that conductivity. In particular, phenomena in the time domain such as anomalous carrier pulse propagation (e.g. Schirmacher 1981) and trapping problems (e.g. Movaghar 1980). The Green's function contains more information than does the mean voltage drop required in the equivalent circuit formulation. It is no surprise then that it is a more difficult quantity to approximate. Nevertheless we have only been concerned with conductivity and Hall mobility; in this context the additional information contained in the Green's function is superfluous.

Consider now the method of calculation that we used to obtain the EPA to $\sigma(\omega)$. In some sense we did not actually achieve a complete analytic theory because we had a parameter κ that was fixed by knowing some numbers obtained previously via computer simulations of percolation problems. The MRWA is a complete analytic theory because the analogous quantity to κ is calculated directly. However the value obtained was shown to be only correct in one special case.

Further research might be directed towards finding an analytic theory that works well in all cases , independently reproducing the percolation exponents. Let us therefore examine possible ways that both the random walk and equivalent circuit approaches could be improved.

The random walk theory has a number of areas in which developments can be made. A more sophisticated summation technique should yield good results without having to make the somewhat ad hoc invokation of the effective medium described in chapter 5. A particularly useful development would be a direct summation of the Green's function's Dyson expansion in an energy dependent model. Alternatively the effective medium formalism could be used with an explicit calculation of the effective rate. However, if the effective medium by association formalism were to be retained, an improved calculation of the self energy $S(\epsilon)$, substituted into the right hand side of equation (5.2.24), should yield better d.c. conductivity exponents.

There are two avenues open for improvement of methods based on the equivalent circuit approach. Firstly, the average admittance $Y(\epsilon)$ is a free parameter in the EPA and may in principle be recalculated in a better approximation than that represented by the mean-field approach in chapter 6; a better exponent should be the result. This is in some way analogous to improving $S(\epsilon)$ above but one should recall that the EPA is derived by a systematic approximation scheme to exact equations whereas equation (5.2.24) is not. The second improvement would relate to the averaging procedure used when the exactly represented external circuit is considered. Recall that we averaged the circuit external to

the pair of sites labelled 1 and 2 over r_{12} and could hence neglect the off-diagonal part, A_{12}, of the two-port admittance matrix. A better approximation would seek to evaluate $A(r_{12},\epsilon_1,\epsilon_2)$, $Y_1(r_{12},\epsilon_1,\epsilon_2)$ and $Y_2(r_{12},\epsilon_1,\epsilon_2)$. It is possible to write down coupled non-linear equations for these quantities through an extension of the mean-field approach that we used for $Y(\epsilon)$. A number of circuit elements are treated exactly and the remainder of the circuit represented by Y's and A's. The equations one obtains are prohibitively complicated and would require excessive amounts of computer time to solve them, with no guarantee of success. Future research should therefore be directed towards seeking a simple way of averaging the external circuit beyond the EPA.

The analytic calculation of the critical percolation quantity s_p, for example in R-hopping via the number N_p, is in itself an interesting problem. Because, as we showed in chapter 3, it is equivalent to a hopping problem, future work on the calculation of S or Y would lead to improved estimates for s_p. As reported in this thesis, the state-of-the-art prediction for R-hopping is $N_p = 1$, for all dimensionality d, in the simple mean field theory and $N_p = e$, for all d, in the MRWA. The EMA of section 5.3 apparently gave some dependence of N_p on d, but this was in fact only a dependence on the lattice coordination number, which varies among the available Bravais lattice types in two and three dimensions. In any case the numbers were not very accurate.

While the above considerations are of immense interest as purely theoretical problems, it is worthwhile remembering that the EPA actually works very well. It thus

allows us to fulful the aim of this thesis that seeks to find a unified conductivity formula through which the validity of the Miller-Abrahams rate equation model can be tested. We investigated this in chapter 7 where we considered hopping conduction in impurity bands and amorphous semiconductors.

The data on impurity conduction that was analysed is, to our knowledge, the sum total of all published data on a.c. hopping conductivity in n-type semiconductors. There is, however, sufficient information for certain inferences to be drawn.

The theory worked quite well for the low compensated doped Silicon investigated by Pollak and Geballe. The input parameter was the density of states and we found only a scale discrepency in the low temperature a.c. conductivity which could be attributed to the somewhat arbitrary choice of a Gaussian density of states. The theory awaits a realistic calculation of the actual shape of $\rho(\epsilon)$ and this is in fact in progress (Cox 1982).

In chapter 7 we also analysed data on n-type Gallium Arsenide. One might suppose that the Miller-Abrahams theory would be prone to less error in this material than in Silicon. This is because the donor wavefunctions are anisotropic in Si and spherically symmetric in GaAs; in the theory the anisotropy is simply averaged over. However we found that although good agreement was obtained for the d.c. conductivity, the theory did not predict an a.c. conductivity higher than $\sigma(0)$ at the frequencies where it was observed. The experimental a.c. conductivity depends on the site density so that one might infer a polarizability associated with the impurity states, ~~additional~~ additional to the

mechanism we have considered. One could therefore seek to isolate such an effect and calculate its contribution to $\sigma(\omega)$. However the accuracy of our d.c. conductivity results may be an accident of two or more inaccuracies cancelling out. We isolated two possible sources of inaccuracy in the theory. ~~Firstly~~ Firstly, the polar nature of GaAs implies an electron-phonon coupling additional to the deformation potential interaction assumed by Miller and Abrahams. Secondly the value of compensation ratio, $K \cong 0.5$, suggests Coulomb interactions between the charge carriers could be important. The formulation of a many-body theory of impurity conduction is a great challenge for future research. It is difficult to immediately comprehend what form such a theory would take. Butcher (1982) suggests that that if the site occupation probability representation were to be retained then one could replace the transition rates in the rate equations by a memory kernel and the right hand side of equations (1.1) would include a convolution in time. This implies that, in frequency space, an identical formalism to the one that we have considered would be obtained, except that we would have a frequency dependent effective rate. The EPA is then available as a solution to the linearised rate equations, but the calculation of the appropriate frequency dependent rate remains a formidable problem.

The amount of experimental data presently available is really insufficient to allow us to identify precisely the conditions under which the simple Miller-Abrahams theory of impurity conduction breaks down. In the light of the above discussion we are immediately led to suggest that, if possible, measurements of a.c. conductivity in low compensation GaAs and Si with $K \cong 0.5$ should be performed.

It is worth reiterating that the application of the Miller-Abrahams theory to conduction in amorphous semiconductors is quite ad hoc. The structure of the electron and phonon states in these materials is undoubtably more complex than in an impurity band. Neverthless, the conductivity phenomena observed are quite similar to impurity conduction. However we have observed that the quantitative predictions of the rate equations model are not realistic. A tractable goal for an improved theory of conduction in the amorphous case might be rate equations with more appropriate transition rates. Miller and Abraham's assumption of hydrogenic states coupled by a deformation potential interaction to phonons whose energy spectrum are those of phonons in a pure crystal is surely not appropriate.

A new sphere of application for the rate equation model is provided by the new material polyacetylene which, when doped, is expected to show thermally activated hopping at low temperatures. Kivelson (1982) has performed some preliminary investigations; he uses the pair approximation to discuss a.c. conductivity. An immediate application of the EPA would be in an extension of his calculations.

We have developed a simple unified theory of a.c. and d.c. hopping conductivity, the EPA. Its accuracy has been verified and we have used it to analyse some experimental data. Various problems have been isolated which relate to approximations intrinsic to our starting formalism; the Miller-Abrahams rate equation model. Further reseach could concentrate on some theoretical problems encountered in the method of solution of the equations and on the calculation of the transition rates that relate them to phenomena in

real systems.

REFERENCES

Aldea A., Banyai L. and Capek V. 1976 Czech J. Phys B26 717.

Aldea A., Banyai L. 1978 preprint.

Allen F.R. and Adkins C.J. 1972 Phil. Mag. 26 1027.

Ambegaokar V., Halperin B.I. and Langer J.S. 1971 Phys. Rev. B 4 2612.

Amitay M. and Pollak M. 1966 Proc. 8th Int. Conf: Physics of Semicond., ed. Hatoyama (Tokyo, Phys. Soc. Jap.) p549.

Anderson P.W. 1958 Phys. Rev. 109 1492.

Barker J. R. 1976 J. Phys. C 9 4397.

Blakemore J.S. 1967 Semiconductor Statistics (Oxford: Pergamon Press)

Boettger H., Bryksin V.V. and Yashin G.Y. 1979 J. Phys. C. 12 3951.

Boettger H. and Bryksin V.V. 1977 Phys. Stat. Sol. 80 569.

Bryksin V.V. 1980 Sov. Phys. Solid State 22 1421.

Butcher P.N. 1974 J. Phys. C 7 2645.

Butcher P.N. 1975 J.Phys. C 8 L324.

Butcher P.N. 1976 in Linear and Non-linear Electron Transport in Solids eds. J.T. DeVreese and V.E. van Doren (New York: Plenum Press) p.341.

Butcher P.N. 1980 Phil. Mag. B 42 799.

Butcher P.N. 1982 Private Communication.

Butcher P.N. and Hayden K.J. 1977 Phil. Mag. 36 655.

Butcher P.N. and Hayden K.J. 1977b Proc. Sixth Int. Conf. on Amorphous and Liquid Semicond. ed. Kolomiets (Leningrad: Nauka) p89.

Butcher P.N. and Kumar A.A. 1980 Phil. Mag. B 42 201.

Butcher P.N. and Ries B. 1981 Phil. Mag. B 44 179.

Butcher P.N. and McInnes J.A. 1978 Phil. Mag. B 37 249.

Butcher P.N. and McInnes J.A. 1981 Journal de Physique supplement 10 p91.

Butcher P.N. and Morys P.L. 1973 J. Phys. C 6 2147.

Butcher P.N. and Summerfield S. 1981 J. Phys. C 14 L1099.

Butcher P. N., Hayden K.J. and McInnes J.A. 1977 Phil. Mag. 36 19.

Butcher P. N., Hayden K.J. and McInnes J.A. 1979
Phil. Mag. B 39 357.

Capek V. 1972 J. Phys. B 22 1122.

Capek V. 1973 Phys. Stat. Sol. B 60 K5.

Capek V. 1975 J. Phys. C 8 479.

Cox I.D. 1982 Private Communication.

Elliott R.J., Krumhansl J.A. and Leath P.L. 1974
Rev. Mod. Phys 46 465.

Essam J.W., Sondheimer E.H. and Place C.W. 1974
J. Phys. C 7 1258.

Friedman L. and Pollak M. 1978 Phil. Mag. B 38 173.

Friedman L. and Pollak M. 1981 Phil. Mag. B 44 487.

Fritzche H. 1958 J. Chem. Phys. Solids 6 69.

Gel'mont B.L., Gadzhiev A.R., Shklovskii B.I., Shlimak I.S.
and Efros A.L. 1975 Sov. Phys. Semicond. 8 1949.

Gilbert M.H. and Adkins C. 1976 Phil. Mag. 34 143.

Gochanour C.R., Andersen H.C. and Fayer M.D. 1979
J. Chem. Phys. 70 4254.

Golin S. 1963 Phys. Rev. 132 178.

Gruenewald M., Mueller H. and Wuertz D. 1982 to be
published in Solid State Comm.

Hayden K.J. 1978 Ph.D. Thesis (University of Warwick).

Hayden K.J. and Butcher P.N. 1978 Phil. Mag. B 38 603.

Hearn C.J., McInnes J.A. and Butcher P.N. 1982 to be
published in J. Phys. C.

Holstein T. 1961 Phys. Rev. 124 1329.

Kahlert H. 1976a J. Phys. C 9 491.

Kahlert H., Landwehr G., Schlachetzki A. and Salow H. 1976b
Z. Phys B 24 361.

Kesten H. 1980 Comm. Math. Phys. 74 41.

Kirkpatrick S. 1973 Rev. Mod. Phys. 45 574.

Kirkpatrick S. 1979 in Ill-Condensed Matter eds. R.Balian,
R.Maynard and G.Toulouse p.321 (Amsterdam: North-Holland).

Kivelson S. 1982 Phys. Rev. B 25 3798.

Klafter J. and Silbey R. 1980 Phys. Rev. Lett. 44 55.

Long A.R. 1980 Private Communication.

Long A.R. and Balkan N. 1979 Proc. Int. Conf. on amorphous and Liquid Semicond., Cambridge/Mass.

McInnes J.A. 1982 Private Communication.

McInnes J.A. and Butcher P.N. 1979 Phil. Mag. B 39 1.

McInnes J.A., Butcher P.N. and Clark J.D. 1980 Phil. Mag. B 41 1.

Matsubara T. and Toyozawa Y. 1961 Prog. Theo. Phys. 26 739.

Miller A. and Abrahams E. 1960 Phys. Rev. 120 745.

Moraal H. 1982 J. Phys. C 15 L55.

Mott N.F. 1969 Phil. Mag. 19 835.

Mott N.F. and Twose W.D. 1961 Adv. Phys. 10 107.

Mott N.F. and Davis E.A. 1979 Electronic Processes in Non-Crystalline Materials (2nd. Ed.) (Oxford: Clarendon Press)

Movaghar B. 1980 J. Phys. C 13 4915.

Movaghar B. and Schirmacher W. 1981 J. Phys C 14 859.

Movaghar B., Pohlmann B. and Schirmacher W. 1980a Phil. Mag. B 41 49

Movaghar B., Pohlmann B. and Schirmacher W. 1980b Solid State Comm. 34 451

Movaghar B., Pohlmann B. and Sauer G.W. 1980c Phys. Stat. Sol. B 97 533.

Movaghar B., Pohlmann B. and Wuertz D. 1981 J. Phys. C 14 5127.

Odagaki T. and Lax M. 1981 Phys. Rev. B 24 1742.

Odagaki T. and Yonezawa F. 1978 J. Phys. Soc. Jap. 45 693.

Pike G.E. and Seager C.H. 1974 Phys. Rev. B 10 1421

Pollak M. 1972 J. Non-Cryst Solids 11 1.

Pollak M. and Geballe T. H. 1961 Phys. Rev. 122 1742.

Schirmacher W. 1981 Solid State Comm. 39 893.

Scher H. and Lax M. 1973 Phys. Rev. B 7 4491 and 4502.

Shante V.K.S. and Kirkpatrick S. 1971 Adv. Phys. 20 325.

Shklovskii B.I. 1973 Sov. Phys. Semicond. 6 1053.

Shklovskii B.I. and Efros A.L. 1980 Sov. Phys. Semicond. 6 1053.

Stinchcombe R.B. 1973 J. Phys. C 7 179.

Straley J.P. 1981 Private Communication.

Summerfield S. and Butcher P.N. 1981 J. Phys. C 14 L585.

Summerfield S. and Butcher P.N. 1982 to be published.

Sykes M.F. and Essam J.W. 1964 J. Math. Phys 5 1117.

Yonezawa F. and Odagaki T. J. 1978
Solid State Comm. 27 1199 and 1203.

Wierman J.C. 1981 Adv. Appl. Prob. 13 298.

Zvyagin I.P. 1980 Phys. Stat. Sol. B 97 143.

APPENDIX A - ANALYTIC APPROXIMATION TO R-INTEGRALS OCCURRING IN CONDUCTIVITY FORMULAE

The following form of integral occurs in the r-intergals in the various conductivity formulae that have been encountered in this thesis:

$$I_\nu^n = \int_0^\infty \frac{x^n dx}{1 + Z\exp(x - \nu\ln x/2)} \qquad (A.1)$$

where Z is in general a complex number. When |Z| is large a good approximation is

$$I_n^\nu \cong H_n^\nu = \frac{1}{Z}\left[\frac{1}{2}\right]^\nu \Gamma(n + \nu + 1) \qquad (A.2)$$

when $|Z| \to 0$ we separate (A.1) into real and imaginary parts

$$I_n^\nu = \int^\infty x^n f_1(x)dx - i\int^\infty x^n f_2(x)dx \qquad (A.3)$$

where

$$f_1(x) = \frac{1 + s\exp(x')}{[1 + s\exp(x')]^2 + t^2\exp(2x')} \qquad (A.3)$$

$$f_2(x) = \frac{t\exp(x')}{[1 + s\exp(x')]^2 + t^2\exp(2x')} \qquad (A.4)$$

where $Z = s + it$ and $x' = x - \nu\ln x/2$. f_1 is approximately unity for $x' < x'_c$ and exponentially decays above x'_c where

$$x'_c = -\frac{1}{2}\ln(s^2 + t^2)$$

We therefore put

$$f_1(x') = \theta(x' - x'_c)$$

We notice also that $f_2(x)$ is sharply peaked and replace it by

$$f_2(x') = k\delta(x' - x_c')$$

the normalisation k is fixed by

$$k = \int f_2(x')dx' = \tan^{-1}\left[\frac{t}{s}\right]$$

We use these approximations in (A.3). For the real part we notice that $f_1(x)$ is a step function at x_c which satisfies

$$x_c = x_c' + \nu \ln x_c/2 \qquad (A.5)$$

we have found that the solution to second order in ν is always accurate enough for our purposes:

$$x_c = x_c' + \nu \ln[(x_c' + \nu \ln x_c'/2)/2)] \qquad (A.6)$$

for the imaginary part we change variables in (A.3) to x' and to first order in ν we find

$$x^n dx = (x'^n + nx'^{n-1}\nu \ln x'/2 + \nu x'^{n-1})dx'$$

These results lead to

$$I_n^\nu \cong L_n^\nu = x_c^{n+1}/n+1 - i\tan^{-1}\left[\frac{t}{s}\right](x_c'^n + nx_c'^{n-1}\nu \ln x_c'/2 + \nu x_c'^{n-1})$$

To decide when to use H_n^ν rather that L_n^ν we found the value of x_c' that minimises H_n^ν/L_n^ν, when Z is real, $x_c'(\min)$, and used H_n^ν for $x_c' < x_c'(\min)$. Values of $x_c'(\min)$ are found numerically; the results for various n and ν are given in table 1.

The accuraccy of this type of approximation for the pair approximation has been verified by Butcher and Ries (1981). Furthermore we have used it to recalculate the d.c.

n	1	2	3	4	5
ν 0	2.0	3.0	4.0	5.0	6.0
3/2	2.631	3.375	4.185	5.047	5.949
2	2.710	3.412	4.203	5.051	5.954

TABLE 1

Values of the optimum change-over parameter, x'_c(min), in the choice of approximation to I_n^ν for various n and ν values.

conductivity for the energy dependent model discussed in chapter 6. Fig. 20 shows that the error involved is very small.

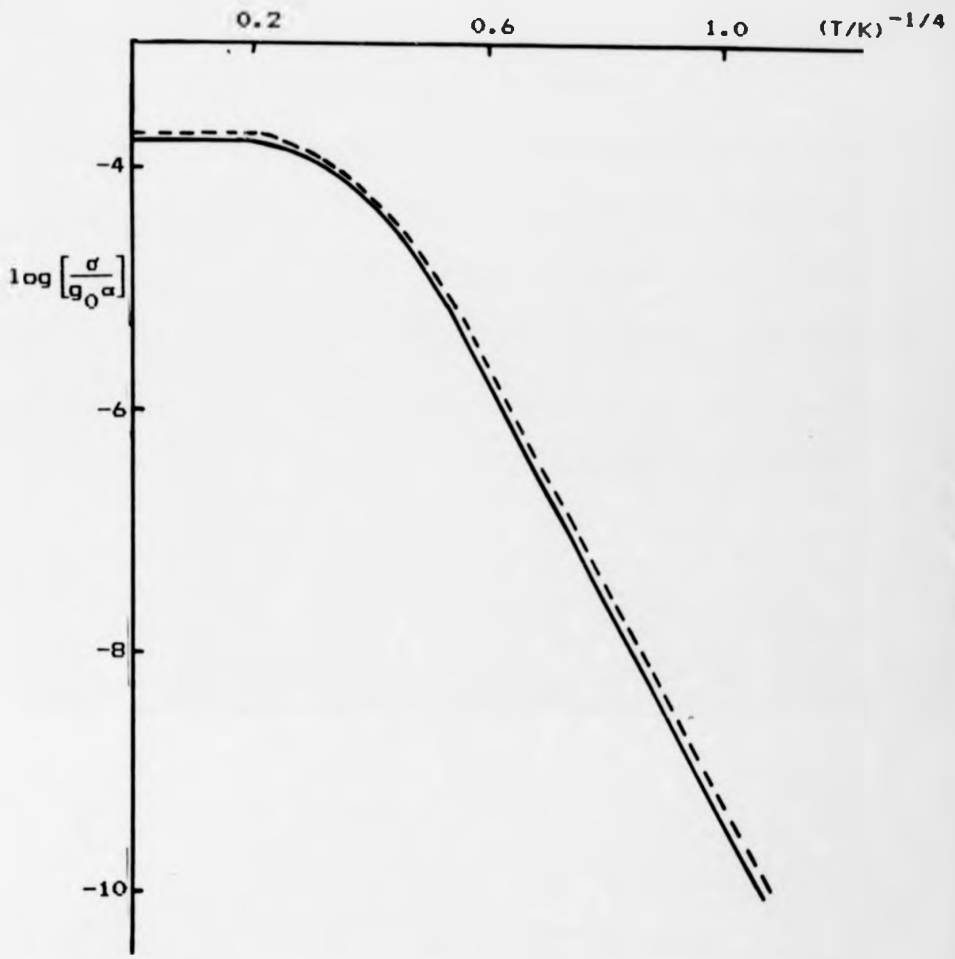


FIGURE 20

Accuracy of the analytic approximation to the r-integrals in the conductivity formulae. The results of calculations of the EPA for the energy dependent model considered in section 6.5 are plotted. The full curve is the result obtained when the approximations are used and the dashed curve is the full numerical calculation, as plotted in figure 10.

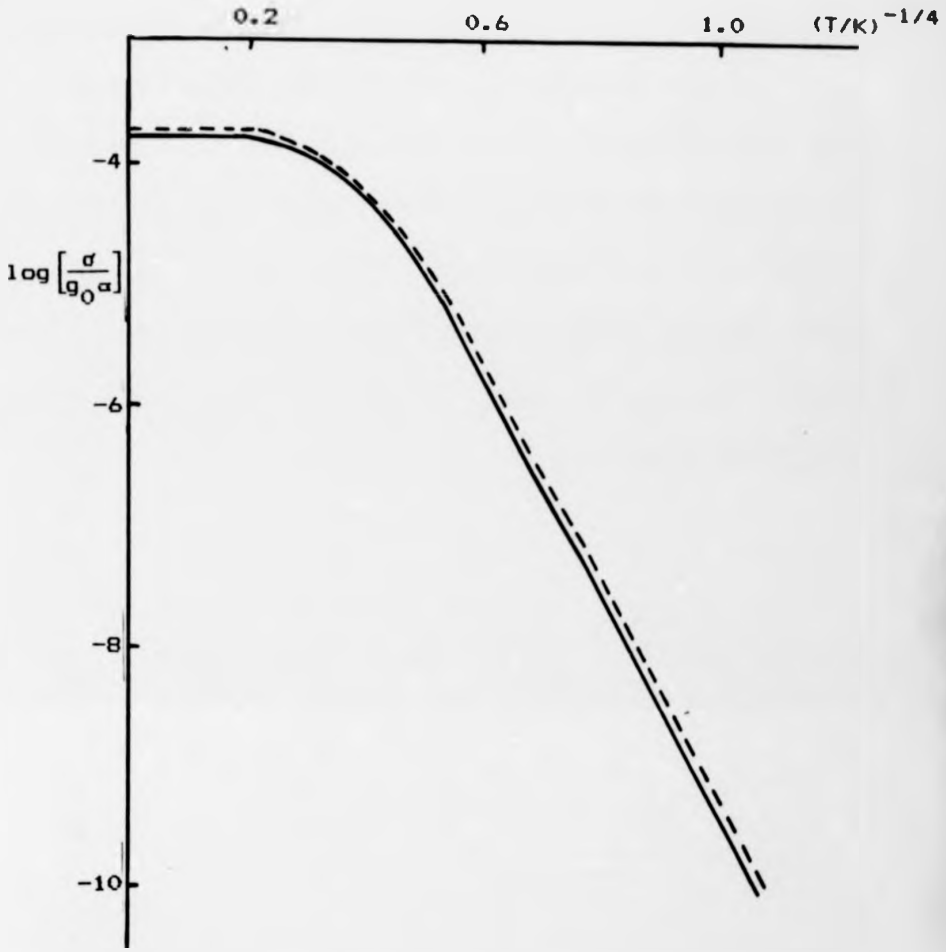


FIGURE 20

Accuracy of the analytic approximation to the r-integrals in the conductivity formulae. The results of calculations of the EPA for the energy dependent model considered in section 6.5 are plotted. The full curve is the result obtained when the approximations are used and the dashed curve is the full numerical calculation, as plotted in figure 10.